# NOVEL VISUALIZATION AND ALGEBRAIC TECHNIQUES FOR SUSTAINABLE DEVELOPMENT THROUGH PROPERTY INTEGRATION

A Dissertation

by

VASILIKI KAZANTZI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2006

Major Subject: Chemical Engineering

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December 2006

Major Subject: Chemical Engineering

## ABSTRACT

Novel Visualization and Algebraic Techniques for Sustainable Development Through Property Integration. (December 2006)

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Chair of Advisory Committee: Dr. Mahmoud M. El-Halwagi

The process industries are characterized by the significant consumption of fresh resources. This is a critical issue, which calls for an effective strategy towards more sustainable operations. One approach that favors sustainability and resource conservation is material recycle and/or reuse. In this regard, an integrated framework is an essential element in sustainable development. An effective reuse strategy must consider the process as a whole and develop plant-wide strategies. While the role of mass and energy integration has been acknowledged as a holistic basis for sustainable design, it is worth noting that there are many design problems that are driven by properties or functionalities of the streams and not by their chemical constituency. In this dissertation, the notion of componentless design, which was introduced by Shelley and El-Halwagi in 2000, was employed to identify optimal strategies for resource conservation, material substitution, and overall process integration.

First, the focus was given on the problem of identifying rigorous targets for material reuse in property-based applications by introducing a new property-based pinch analysis and visualization technique. Next, a non-iterative, property-based algebraic technique, which aims at determining rigorous targets of the process performance in material-recycle networks, was developed. Further, a new property-based procedure for determining optimal process modifications on a property cluster diagram to optimize the allocation of process resources and minimize waste discharge was also discussed. In addition, material substitution strategies were considered for optimizing both the process and the fresh properties. In this direction, a new process design and molecular synthesis

methodology was evolved by using the componentless property-cluster domain and Group Contribution Methods (GCM) as key tools in developing a generic framework and systematic approach to the problem of simultaneous process and molecular design.

To my son, Stavros

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# CHAPTER I
# INTRODUCTION

The efficient use of process resources is recognized as a key element of sustainable development and an effective strategy for cost reduction and environmental acceptability in the process industries. Resource conservation strategies have been playing a major role in establishing cost-effective production policies, as well as environmental benign practices. Recycle/reuse of process resources has been recognized as an effective approach toward resource conservation, which constitutes a first step to a no/low cost in-plant implementation strategy for sustainable development.

Moreover, process design solutions, which consider material recycle/reuse, have been found particularly successful, when they were established on a plant-wide basis and in a holistic way (Dunn and El-Halwagi, 2003). Thus, process integration has been acknowledged as the holistic approach to process design and optimization, which makes use of the unity of the process and helps developing systematic, fundamental and generally applicable techniques for optimal design. The first breakthrough in process integration was the development of heat integration (Linnhoff and al., 1982), which aimed at designing optimal process systems by optimizing the heat exchange and the utilization of fuel, power and pressure. A major contribution in this area was the development of the thermal pinch analysis, which is considered the definitive way of optimizing heat exchange networks. Later, mass integration has emerged with the development of the mass pinch analysis by El-Halwagi and Manousiouthakis, 1989, who provided the basis for targeting mass exchange among rich and lean streams in complex systems.

A remarkable attribute of process integration is its ability to benchmark performance targets for the overall system, no matter how complex it is. These performance targets can be identified ahead of any detailed design and without commitment to the specific

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This dissertation follows the style and format of the Chemical Engineering Science.

details of the strategies that lead to process improvement. In particular, process design methodologies are usually cumbersome and iterative in nature, and as such they are often time-consuming and computationally detailed. Thus, targeting becomes a very powerful tool, which alleviates this drawback in the beginning of the design approach. By employing such a targeted approach, the design targets can be identified a priori, and then any design scheme that matches these targets or the next best one constitutes the optimum design solution. In this work, new system-based targeting techniques, which use visualization tools, algebraic procedures and mathematical programs, are developed.
Recently, significant progress has been made in the optimization of material recycle and reuse. In particular, mass integration has been employed as an effective and holistic framework that aims at optimizing the allocation, generation and separation of streams and species throughout a process. Extensive work and reviews in the area of mass integration can be found in the literature (e.g. El-Halwagi, 1997, 1998; El-Halwagi and Spriggs, 1998; Dunn and El-Halwagi, 2003, Wang and Smith, 1994; Dhole et al., 1996; Sorin and Bédard, 1999; Polley and Polley, 2000; Bagajewicz and Savelski, 2001; Savelski and Bagajewicz 2000a,b, 2001; Zhou et al., 2001; Alves and Towler, 2002; Hallale, 2002; El-Halwagi et al., 2003; Hamad and Fayed, 2004; Manan et al., 2004; Foo et al., 2005; Aly et al., 2005; Almutlaq et al., 2005).

In spite of the importance of the mass integration techniques for material recycle/reuse, these are limited to address problems that are represented and addressed by only one property, namely the composition of the components and process streams in the system. However, other properties (or functionalities) such as density, viscosity, reflectivity, turbidity, color and vapor pressure can be considered in optimizing a process system. In addition, many design constraints on material recycle are governed by properties and not only by chemical components. Hence, there is a need for a new property-based design framework that is generic, and does not necessarily depend on the chemical constituency of the system (non-chemocentric). In this regard, a systematic framework for representing and addressing such design problems that are driven by properties has been developed by Shelley and El-Halwagi, 2000, who introduced the

property clustering notion in order to methodically track properties throughout a processing system. Property clusters are tailored to exhibit intra- and inter-stream conservation patterns, thus enabling the implementation of linear additive rules and ternary representations. Later, El-Halwagi et al., 2004, generalized this newly developed component-less design framework to generate the so-called property integration area, which focuses on the property-based holistic approaches to the allocation and manipulation of streams and processing units, which is based on tracking, adjustment, and matching of functionalities throughout the process.

The work presented in this dissertation employs the property integration principals to generate new graphical and algebraic techniques for resource conservation and performance optimization. The property-based additive rules developed within the property integration framework are used to first represent and formulate the property-driven design problem, which is then addressed by directly determining targets for minimum use of fresh resource, maximum recycle of process streams and minimum waste discharge, along with valuable insights on process modifications. In addition, cluster-based ternary diagrams are used to explore how changes in the process design and operating conditions can further improve the process performance. Finally, the problem of simultaneous process and molecular design is examined here from a property perspective. It employs both group contribution methods and clustering techniques to integrate and inter-relate important property-based features and inputs from both areas. The problem was decomposed using a reverse formulation, which enables property-based process constraints to be considered in the molecular design problem.

The new property integration framework unifies the design methodologies considered in this work, and enables the development of new targeting techniques including graphical procedures, algebraic approaches and mathematical programs. This work demonstrates the utility of the property-based framework to examining novel and alternative pathways to process and molecular design, which can promote sustainability and facilitate numerous applications in environmental design, solvent substitution, resource conservation and product quality management.

# CHAPTER II
# PROBLEM STATEMENT

The overall problem considered in this work can be state as follows.

A process with a number of process sinks (units) $N_{sinks}$ is considered. Each sink, j, requires a feed with a given flow rate, $G_j$, and an inlet property, $p_j^{in}$ that satisfies the following constraint:

$$p_j^{\min} \le p_j^{in} \le p_j^{\max} \qquad \text{where j = 1,2, …, } N_{sinks} \tag{2.1}$$

where $p_j^{\min}$ *and* $p_j^{\max}$ are the specified lower and upper bounds on admissible property to unit *j*.

The plant has a number of process sources (e.g., process and waste streams), $N_{sources}$ that can be considered for possible reuse and replacement of the fresh material. Each source, *i*, has a given flow rate, $F_i$, and a given property, $p_i$.

Available for service is a fresh (external) resource whose property value is $p_{Fresh}$ and can be purchased to supplement the use of process sources in sinks. First, the objective is to develop a systematic visual approach and then a non-iterative algebraic procedure, which can a priori determine the target for minimum usage of the fresh resource, maximum material reuse, and minimum discharge to waste. The problem can be schematically represented through a source-sink allocation as shown in Fig. 1. According to this representation, each source is allowed to split and be forwarded to all sinks. In particular, the objective here is to determine the optimum flow rate from each source to each sink so as to minimize the consumption of the fresh resource, as well as the targets for minimum fresh consumption and minimum waste discharge.

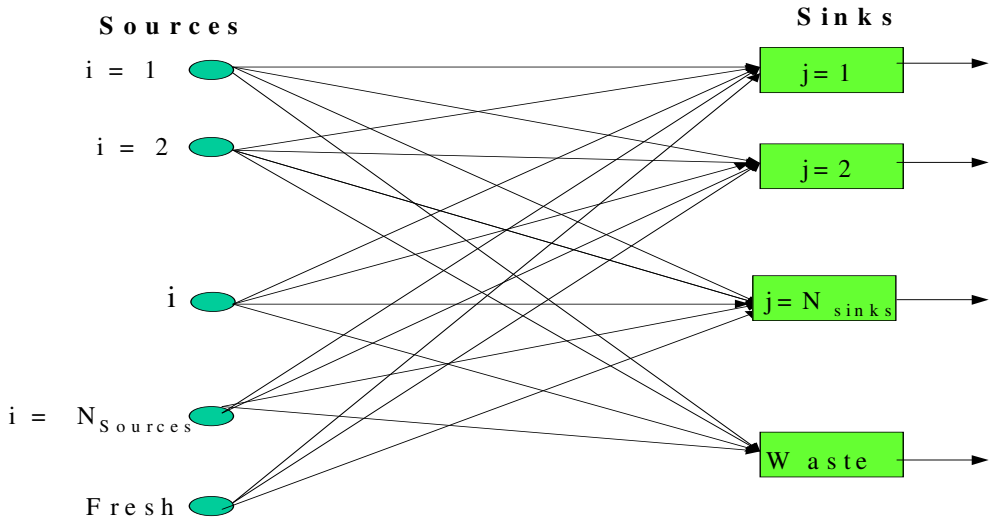


Fig. 1. Schematic representation of the property-based material reuse problem.

In addition, the aforementioned problem can be extended to include more properties (up to three for graphical solutions) that can adequately characterize the system and the recycle/reuse problem specifications. In this case, process and waste streams possess a finite number of properties, $N_p$, which for visualization purposes need to be here limited to three. However, it is worth mentioning that the same problem statement would hold for more properties, for which mathematical programming techniques need to be employed in order to obtain a design solution to the problem with the same mathematical formulation.

The problem that deals with more than one property has already been discussed before (Shelley and El-Halwagi, 2000, El-Halwagi et al, 2004, Qin et al., 2004, Eden et al., 2002 and 2004, Eljack et al., 2005). Nevertheless, in these previous papers, sources have been represented as static nodes on the ternary cluster diagrams. In reality, though, process sources may come from different units and mixtures of streams, and are in fact functions of the process variables. Thus, it is possible to make changes in the process conditions, and examine how these changes may affect and further improve the material

recycle/reuse options. In this regard, each property value of a stream $i$, $p_i$, is a function of a set of design variables, $\mathbf{d}_{p,i}$ and a set of operating variables, $\mathbf{r}_{p,i}$ charactering the whole process. The design variables are allowed to take values from a specific vector interval $[\mathbf{d}^{l}_{p,i}, \mathbf{d}^{u}_{p,i}]$ dictated by design restrictions throughout the process. Similarly, the operating variables belong to another interval $[\mathbf{r}^{l}_{p,i}, \mathbf{r}^{u}_{p,i}]$ posed by operating constraints throughout the system, e.g.

$$\mathbf{d}^{l}_{p,i} < \mathbf{d}_{p,i} < \mathbf{d}^{u}_{p,i} \tag{2.2}$$

$$\mathbf{r}^{l}_{p,i} < \mathbf{r}_{p,i} < \mathbf{r}^{u}_{p,i} \tag{2.3}$$

where $p$= 1, 2, …, Np and $i$ = 1, 2, …, $N_{sources}$

The graphical representation of the aforementioned problem is given in Fig. 2.

The specific objective of this problem is to identify optimal process modification strategies in order to optimize a process objective, while satisfying all property constraints. Additionally, new fresh substitution options are to be considered by optimizing the process variables and properties of the streams.

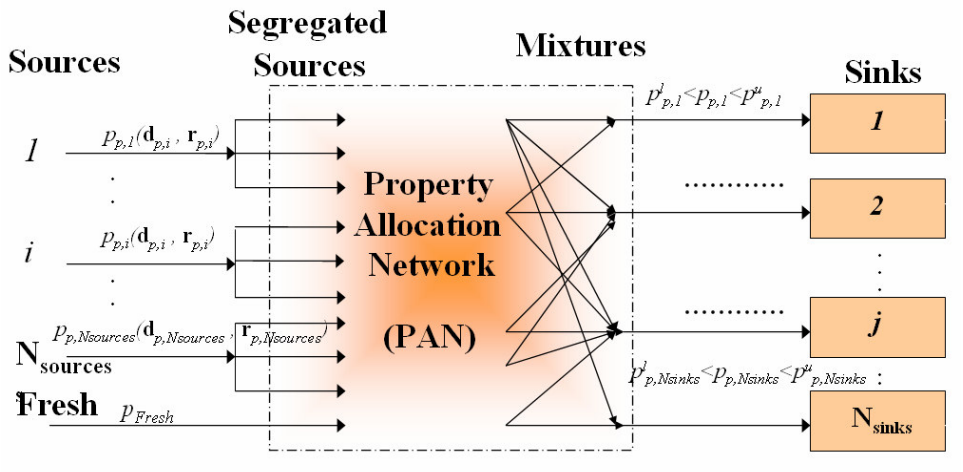


Fig. 2. Schematic representation of the property-based allocation and interception problem.

The process design problem of material recycle/reuse, which is described above, can be methodically coupled with the molecular design problem of synthesizing fresh resource molecules with desirable properties for enhanced process performance. Property integration provides a natural environment for integrating process and molecular design, and can significantly assist the search of new fresh molecules with the exact properties needed for achieving the optimum material recycle/reuse. In addition to the aforementioned process design problem statement, the problem of simultaneous process design and material synthesis considers a number of functional groups, $N_G$, based on the group contribution method classification (Marrero, J. and R. Gani, 2001). Each functional group, $g$ ($g$=1, 2,…, $N_G$), has a given property contribution, $gc_{p,g}$ to the property values of potentially synthesized molecules. Further objective of this part of the work is to optimize the material recycle by synthesizing optimum feasible molecules that can be used to supplement the usage of process sources in the sinks, while satisfying all process constraints.

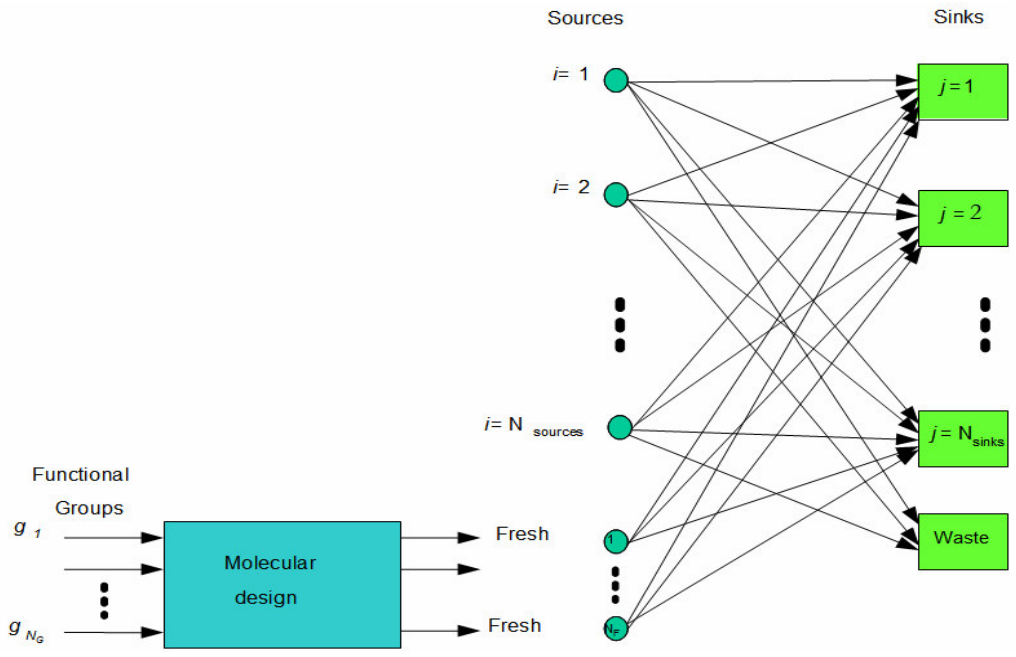


Fig. 3. Schematic representation of the simultaneous process and molecular design.

# CHAPTER III
# TARGETING DIRECT MATERIAL REUSE THROUGH PROPERTY INTEGRATION – A VISUALIZATION TOOL

## 1. INTRODUCTION

As mentioned in Chapter I, many material reuse problems are driven and governed by properties or functionalities of the streams and not by their chemical constituency. For instance, the selection of solvents is typically based on properties such as equilibrium distribution coefficients, viscosity and volatility. It is worth noting that the quality of many products and intermediates is described in terms of properties. Hence, in recycling/reusing process and waste streams the properties of those streams must satisfy the requirements of the processing units that can accept them. Additionally, a large number of environmental problems are associated with properties of the discharges. For instance, the extent of environmental emissions is typically linked to properties of the pollutants (e.g. volatility, solubility, etc.). Furthermore, the environmental regulations involve limits on properties (e.g., pH, color, toxicity, TOC, BOD, ozone-depleting ability). Similarly, ecological consequences of the discharged wastes are dependent on the properties of the pollutants.

The foregoing discussion underscores the critical need to develop a systematic design methodology, which is based on properties and functionalities. Property integration is a functionality-based, holistic approach to the allocation and manipulation of streams and processing units, which is based on the tracking, adjustment, assignment, and matching of functionalities throughout the process. Since properties (or functionalities) form the basis of performance of many units, the design techniques must be able to track key properties instead of key compounds. Nonetheless, there is an inherent challenge: while chemical components are conserved, properties are not. Therefore, the question is whether or not it is possible to track these functionalities instead of compositions. The answer is yes! Recent work done by Shelley and El-Halwagi (2000) has shown that it is possible to tailor conserved quantities, called

clusters that act as surrogate properties and enable the conserved tracking of functionalities instead of components. Graphical (Shelley and El-Halwagi, 2000; El-Halwagi et al., 2004), as well as algebraic techniques (Qin et al., 2004) have been developed to foster material reuse using property-based approaches. Additionally, property-based frameworks have been used to integrate process and product design (Eden et al. 2002, 2004; Gani and Pistikopoulos, 2002) and to induce process modifications (Kazantzi et al., 2004a, 2004b).

This chapter focuses on the problem of identifying rigorous targets for material reuse in property-based applications by introducing a new property-based pinch analysis and visualization technique. This technique provides a new systematic approach for optimal resource allocation and waste reduction, and enables the designer to gain valuable insights on process characteristics and modification alternatives using properties or functionalities of the streams as the main "driving force" of the design strategy.

## 2. PROBLEM STATEMENT

To illustrate the problem, consider a process with a number of process units that can serve as sinks ($N_{sinks}$). Each sink, $j$, requires a feed with a mass flow rate, $G_j$, and an inlet property, $p_j^{in}$ that satisfies the following constraint:

$$p_j^{\min} \le p_j^{in} \le p_j^{\max} \qquad \text{where } j = 1,2, \ldots, N_{sinks} \tag{3.1}$$

where $p_j^{\min}$ *and* $p_j^{\max}$ are the specified lower and upper bounds on the property admissible to unit $j$.

The plant has a number of process sources ($N_{sources}$; e.g., process streams, wastes) that can be considered for possible reuse and replacement of the fresh material. Each source, $i$, has a given flow rate, $F_i$, and a given property, $p_i$ ($i = 1, 2, \ldots, N_{sources}$).

Available for service is a fresh (external) resource, with a property value of $p_{Fresh}$ that can be purchased to supplement the use of process sources in sinks.

The objective is to develop a non-iterative graphical procedure that determines the target for minimum usage of the fresh resource, maximum material reuse, and minimum discharge to waste. In addition, the optimum flowrate from each source to each sink is to

be determined, so as to minimize the consumption of the fresh resource and maximize the process material usage.

## 3. PROPERTY-MIXING OPERATORS

When several sources are mixed, the resulting mixture will have a total flowrate of $\overline{F}$ and a mean property of $\overline{p}$, which needs to be evaluated as a function of the flowrate $F_i$ and property $p_i$ of each stream. Consider the following mixing rule for estimating the resulting property of the mixture:

$$\overline{F} * \psi(\overline{p}) = \sum_i F_i * \psi(p_i) \tag{3.2}$$

where $\psi(p_i)$ is the property-mixing operator and $\overline{F}$ is the total flow rate of the mixture which is given by:

$$\overline{F} = \sum_i F_i \tag{3.3}$$

The property-mixing operators can be evaluated from first principles or estimated through empirical or semi-empirical methods. For instance, consider the mixing of two liquid sources whose flowrates are $F_1$ and $F_2$, volumetric flowrates are $V_1$ and $V_2$, and densities are $\rho_1$ and $\rho_2$. Suppose that the volumetric flowrate of the mixture is the sum of the volumetric flow rates of the two streams, i.e.

$$\overline{V} = V_1 + V_2 \tag{3.4}$$

Recalling the definition of density and designating the total flowrate of the mixture by $\overline{F}$, we get

$$\frac{\overline{F}}{\overline{\rho}} = \frac{F_1}{\rho_1} + \frac{F_2}{\rho_2} \tag{3.5}$$

Comparing equations (3.2) and (3.5), we can define the density-mixing operator as:

$$\psi(\rho_i) = \frac{1}{\rho_i} \tag{3.6}$$

Similarly, we can define the operator for other product-related properties, as shown in Table 1. Eq. (3.2) can be applied to a wide range of properties having different patterns of mixing rule. For simplicity, $\psi(p_i)$ will be denoted as $\psi_i$ in the remainder of the text.

Table 1
Indicative property operator expressions

| Property of mixture | Mixing rule | Operator | Reference |
|---|---|---|---|
| Density, $\overline{\rho}$ | $\frac{1}{\overline{\rho}} = \sum_i \frac{x_i}{\rho_i}$ | $\psi(\rho_i) = \frac{1}{\rho_i}$ | Shelley and El-Halwagi (2000) |
| Reid Vapor Pressure, $\overline{RVP}$ | $\overline{RVP} = \sum_i x_i RVP_i^{1.44}$ | $\psi(RVP_i) = RVP_i^{1.44}$ | Shelley and El-Halwagi (2000) |
| Material content, $\overline{M}$ | $\overline{M} = \sum_i x_i M_i$ | $\psi(M_i) = M_i$ | Shelley and El-Halwagi (2000); El-Halwagi et al. (2004) |
| Electric resistivity, $\overline{R}$ | $\frac{1}{\overline{R}} = \sum_i \frac{x_i}{R_i}$ | $\psi(R_i) = \frac{1}{R_i}$ | El-Halwagi et al. (2004) |
| Paper reflectivity, $\overline{R}_\infty$ | $\overline{R}_\infty = \sum_i x_i R_{\infty,i}^{5.92}$ | $\psi(R_{\infty,i}) = \sum_i x_i R_{\infty,i}^{5.92}$ | Eden et al. (2002) Qin et al. (2004) |

We can also rewrite the sink constraints given by equation (3.1) in terms of the property-mixing operator as:

$$\psi_j^{\min} \le \psi_j^{in} \le \psi_j^{\max} \tag{3.7}$$

Next, we define the property load of a stream or a sink as follows:

$$M_i = F_i * \psi_i \tag{3.8}$$

$$M_j = G_j * \psi_j$$

The property load is the product of the flowrate of a source ($F_i$) or a sink ($G_j$) with its associated property operator ($\psi_i$ or $\psi_j$ respectively).

This newly defined parameter provides information similar to the information given by the mass load in the conventional mass integration approach. Note that from equations (3.1) and (3.7), the property of a sink is always bounded within a range of properties or its associated operators. Consequently, due to the constant flowrate required by a sink, the constraints of the sink in equation (3.7) can be rewritten in terms of property loads:

$$M_j^{\min} \le M_j^{in} \le M_j^{\max} \tag{3.9}$$

## 4. OPTIMALITY CONDITIONS

In order to develop the targeting procedure, let us first start with the following special case for which the fresh source has superior properties to all other streams and the sink constraint is given by:

$$\psi_{Fresh} \le \psi_j^{in} \le \psi_j^{\max} \tag{3.10}$$

where

$$\psi_{Fresh} = \psi(p_{Fresh}) \tag{3.11}$$

As mentioned in the previous paragraph, the property load of a sink is defined as the product of the flowrate times the property operator of the feed to the sink. Hence, we can also define the maximum property load for a sink as:

$$U_j = G_j * \psi_j^{\max} \tag{3.12}$$

In deriving the material-reuse targeting procedure, we start by developing a source-sink mapping diagram, where we represent the flowrate versus the property operator for the sources and sinks (Fig. 4).

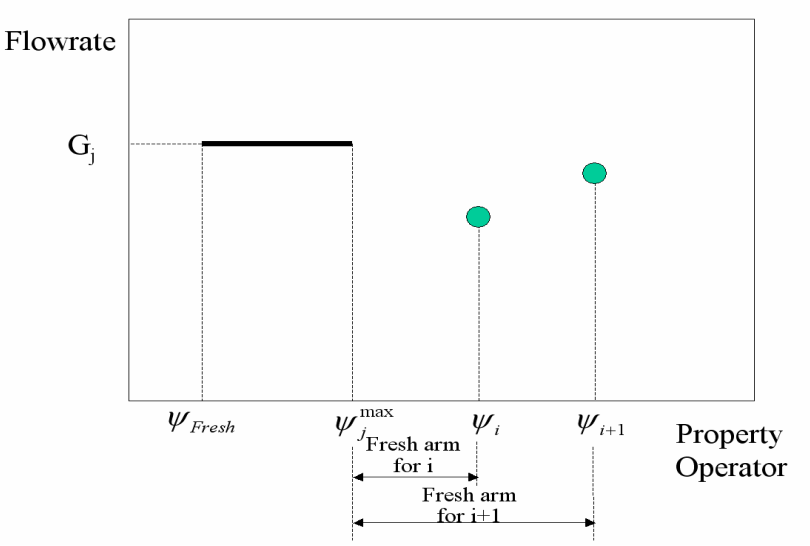


Fig. 4. Property-based source - sink mapping diagram.

For instance, consider a sink *j* whose feasibility constraint for the inlet property to the sink is represented by the horizontal line extending between $\psi_{Fresh}$ and $\psi_j^{\max}$. Instead of using the fresh resource exclusively, let us consider the reuse of process sources *i* and *i*+1 by mixing with the fresh resource. If the fresh stream is mixed with source *i* to yield a feasible inlet property operator for the sink ($\psi_j^{in}$), equation (3.2) can be written as:

$$(F_{Fresh} + F_i) * \psi_j^{in} = F_{Fresh} * \psi_{Fresh} + F_i * \psi_i \tag{3.13}$$

Rearranging, we get

$$\frac{F_{Fresh}}{F_i} = \frac{\psi_i - \psi_j^{in}}{\psi_j^{in} - \psi_{Fresh}} \tag{3.14}$$

Consequently,

$$\frac{F_{Fresh}}{F_i + F_{Fresh}} = \frac{\psi_i - \psi_j^{in}}{\psi_i - \psi_{Fresh}} \tag{3.15}$$

or

$$\frac{F_{Fresh}}{G_j} = \frac{\psi_i - \psi_j^{in}}{\psi_i - \psi_{Fresh}} \tag{3.16}$$

For a given process stream and a fresh resource, the only unknown in the right hand side of equation 3.16 is the inlet property operator to the sink ($\psi_j^{in}$). Hence, for minimum consumption of the fresh resource, the inlet property operator to the sink must be maximized. Since in this case, source *i* lies to the right of the sink, we have the following <u>*sink optimality condition*</u>*:*

***When a fresh source is mixed with a reused material, the inlet property operator to the sink should be assigned to its maximum feasible value, i.e.***

$$\psi_j^{in} = \psi_j^{\max} \tag{3.17}$$

Therefore, for minimum usage of fresh we have

$$\frac{F_{Fresh}}{G_j} = \frac{\psi_i - \psi_j^{\max}}{\psi_i - \psi_{Fresh}} \tag{3.18}$$

In terms of lever-arm rules, we can describe equation (3.18) as

$$\frac{F_{Fresh}}{G_j} = \frac{\text{Fresh arm for } i}{\text{Total arm from } i \text{ to fresh}} \tag{3.19}$$

Fig. 4 illustrates the lever-arm rule.

Similarly, if source *i*+1 is mixed with the fresh we get

$$\frac{F_{Fresh}}{G_j} = \frac{\text{Fresh arm for } i+1}{\text{Total arm from } i+1 \text{ to fresh}} \tag{3.20}$$

Since source *i* has a shorter fresh relative arm than source *i*+1, we should use source *i* before using source *i*+1. Consequently, we get the following <u>*source prioritization rule:*</u>

***The use of the process sources should be prioritized starting with the source having the least value of property operator and sequenced in increasing order of the property operator of the sources.***

## 5. TARGETING PROCEDURE

With the optimality conditions for sources and sinks obtained, we are in a position to develop the graphical targeting procedure. First, we use a property load vs. flowrate representation. The feasibility region for each sink is bounded between the line representing the maximum admissible property operator for that sink and the fresh line (Fig. 5).

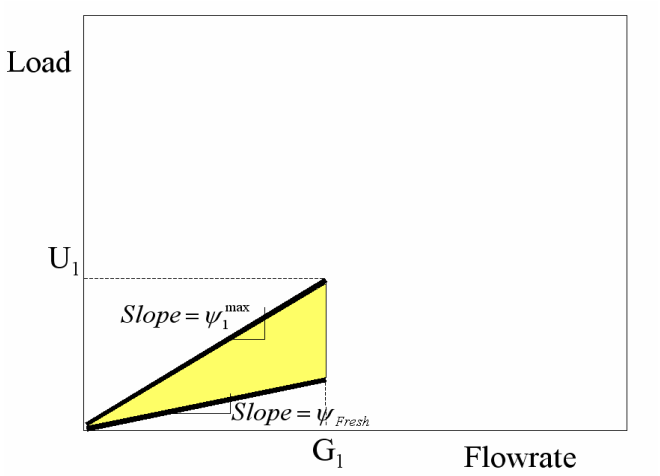


Fig. 5. Feasibility region for a sink.

In order to represent the sources, we start with the source that has the lowest value of property operator in conformance with the source prioritization rule. Then, we can represent the first source as a straight line whose slope is the value of the property operator of the source as shown by Fig. 6. The exact location of this line is not important yet. In the next step, we need to determine its optimal location as part of the targeting procedure.

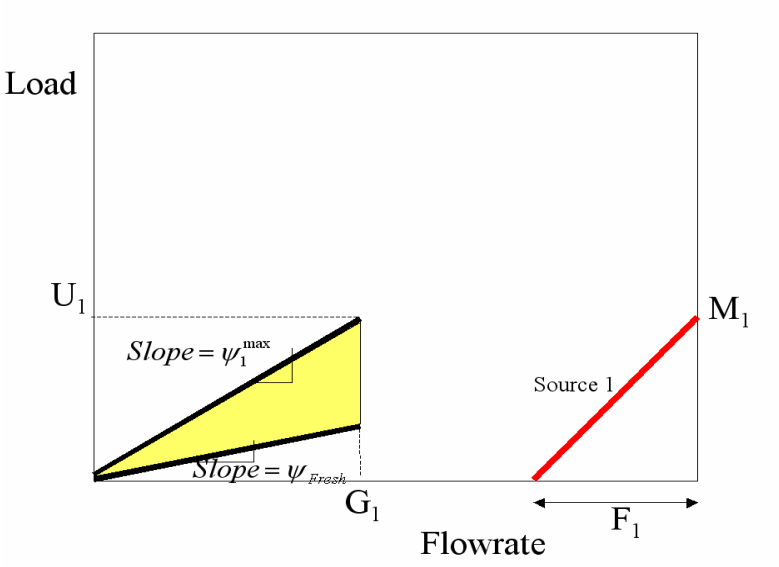


Fig. 6. Sink feasibility region and source representation.

In order to minimize the usage of the fresh resource, we should maximize the reuse of the process source. The mixing of the fresh stream and source 1 can be represented using superposition rule. Source 1 is slid on the fresh line and is pushed to the left, while being completely below the maximum operator line, until source 1 intersects with the maximum operator line of the sink. This defines the maximum utilization of source 1 in the sink and the minimum consumption of the fresh source. This step is shown in Fig. 7.

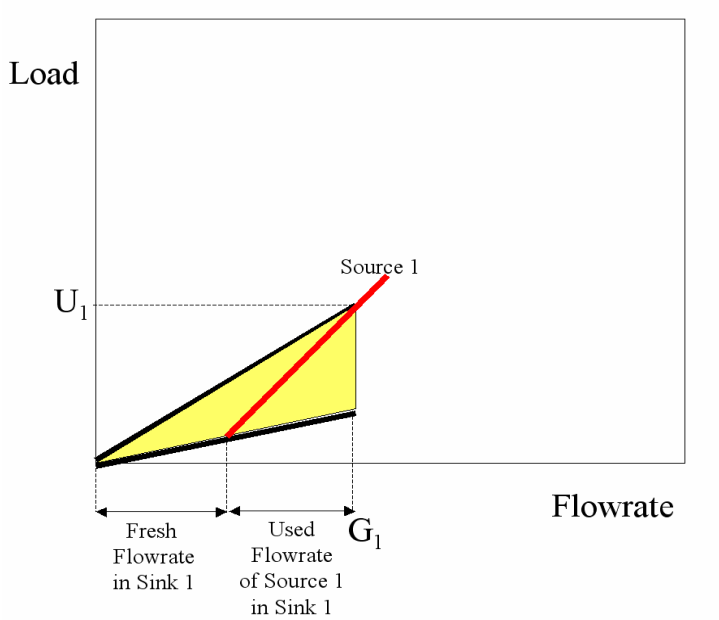


Fig. 7. Sliding source 1 on the fresh line.

Next, we move to the second sink and represent its upper bound constraint using superposition and starting at the end point of sink 1. We also use superposition to add source 2. As can be seen in Fig. 8, we slide the remaining portion of source 1 and source 2 on the fresh line till the source composite intersects with the upper tip of the feasibility region for sink 2. This determines the maximum reuse of sources 1 and 2 and the minimum usage of the fresh resource in sink 2.

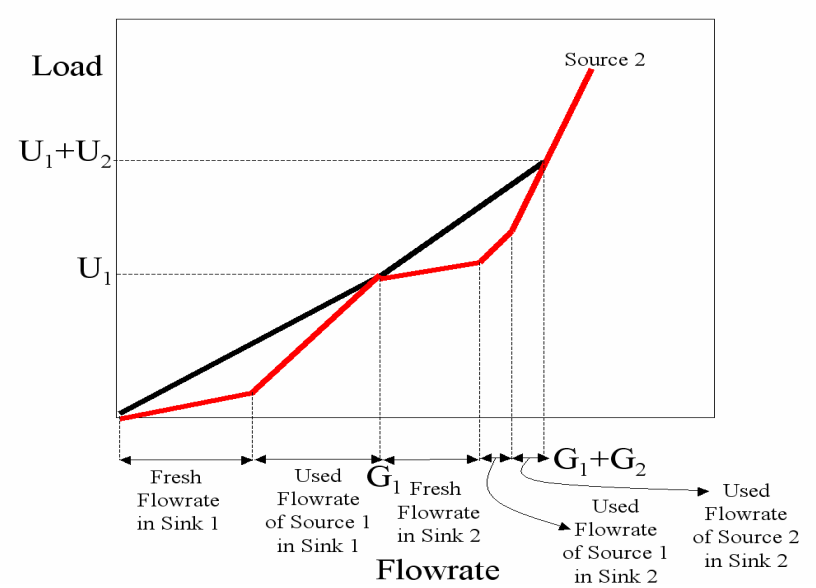


Fig. 8. Developing composites for two sinks and two process sources.

The procedure continues by adding the third sink. As shown by Fig. 9, the remaining portion of source 2 can fulfill the flowrate requirement for sink 3, while the load is completely below that of the sink. Hence, no fresh is needed in sink 3. With no more sources or sinks remaining in the problem, the unused portion of source 2 will be discharged as waste. With maximum reuse of all process sources, this quantity corresponds to the minimum amount of discharged waste.

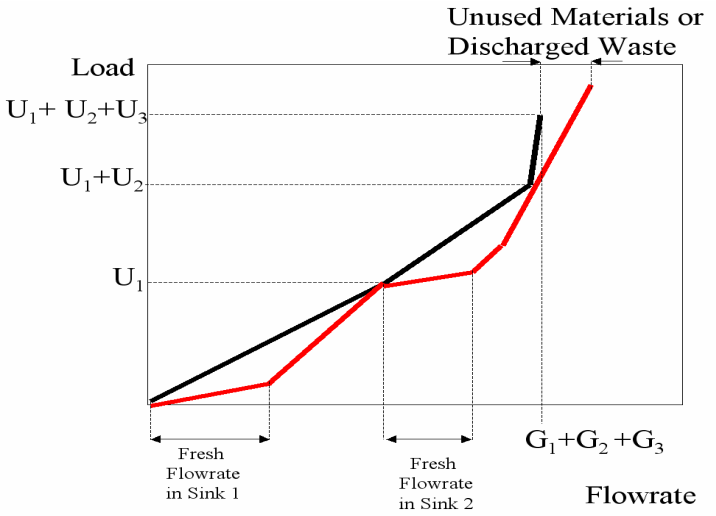


Fig. 9. Representation of all sources and sinks and identification of minimum waste discharge.

A particularly useful observation is that the two linear segments representing the use of the fresh stream in sinks 1 and 2 can be joined to represent the minimum fresh usage in the whole system (Fig. 10). This joining allows for the continuous representation of source 1 followed by source 2. Figure 10 is a novel tool that is referred to as the *property-based material reuse pinch diagram.*

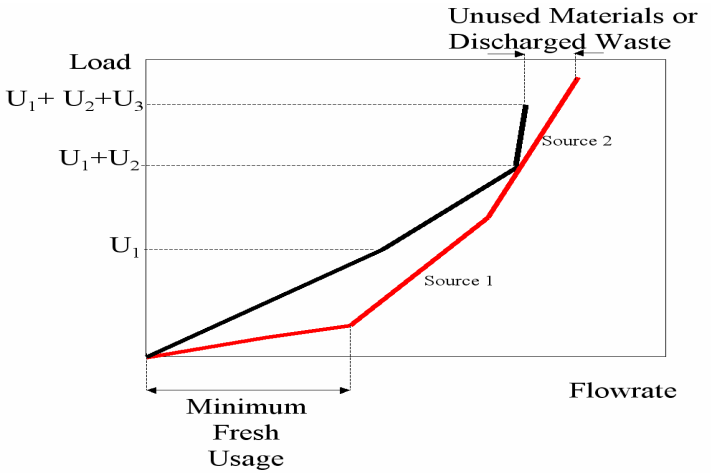


Fig. 10. Combining fresh usages to determine minimum fresh consumption.

We can now summarize the targeting procedure:

1. **Sink Data:** Gather data on the flowrate and acceptable range of targeted property for each sink as in constraint 3.1. Using the admissible range of property value calculate the maximum value of the property operator $\psi_j^{\max}$. Then, evaluate the maximum admissible property load ($U_j$) using equation 3.12. Rank the sinks in ascending order of $\psi_j^{\max}$.

2. **Sink Composite**: Using the required flowrate for each sink ($G_j$) and the calculated values of the maximum admissible loads ($U_j$), develop a representation for each sink in ascending order. Superposition is used to create a sink composite curve.

3. **Fresh Line:** Use equation 3.11 to evaluate the property operator of fresh ($\psi_{Fresh}$). A locus of the fresh line is drawn starting from the origin with a slope of $\psi_{Fresh}$.

4. **Source Data:** Gather data on the flowrate and property value for each process source. Using the functional form of the property operator, calculate the value of the property operator for each source ($\psi_i$). Rank the sources in ascending order of $\psi_i$. Also, calculate the property load of each source ($M_i$) using equation 3.8.

5. **Source Composite**: Using the flowrate for each source ($F_i$) and the calculated values of the property operator ($\psi_i$), develop a representation for each source in ascending order. Superposition is used to create a source composite curve.

The previous steps are represented in Fig. 11.

6. **Pinch Diagram:** The source composite curve is slid on the fresh line pushing it to the left, while keeping it below the sink composite curve, until the two composites touch at the pinch point with the source composite completely below the sink composite in the overlapped region. In this way, we can determine the minimum consumption of fresh resource and the minimum discharge of the waste as shown by the pinch diagram (Fig. 12).

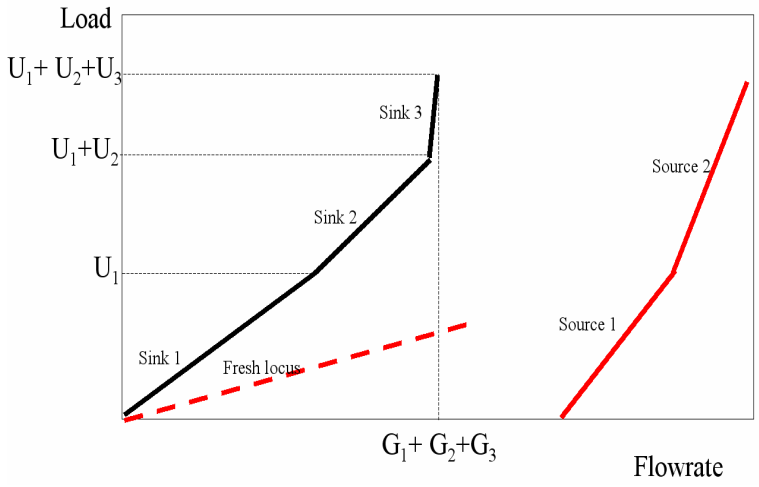


Fig. 11. Developing source and sink composites.

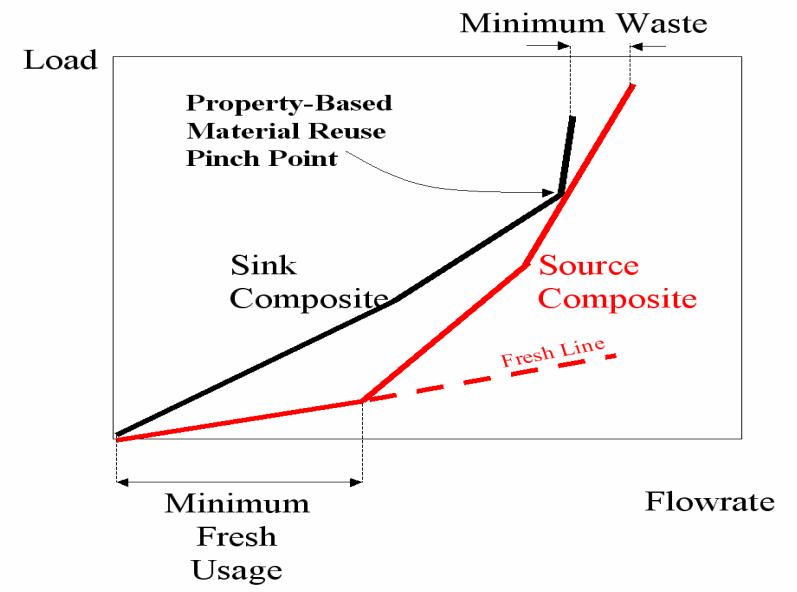


Fig. 12. Property-based material-reuse pinch diagram.

## 6. DESIGN INSIGHTS

*Observations on the property-based material-reuse pinch diagram*

A useful observation can be detected from the material-reuse pinch diagram. The property-based material-reuse pinch point corresponds to the highest point, at which the cumulative flows of the sources equal those of the sinks and the cumulative property loads of the sources equal the maximum allowed by the sinks. The pinch distinguishes two zones. Below that point fresh resource is used in the sinks, whereas above that point unused process sources are discharged. Hence, for the minimum usage of fresh resources, maximum reuse of the process sources and minimum discharge of waste, the following three design rules are needed:

- No property load should be passed through the pinch (i.e. the two composites touch)
- No waste should be discharged from sources below the pinch
- No fresh should be used in any sink above the pinch

The targeting procedure identifies the targets for fresh, waste and material reuse without commitment to the detailed design of the network matching the sources and sinks. In detailing the solution, there can be more than one solution satisfying the identified targets. One solution can be obtained though the procedure shown in Fig. 9. To compare the multiple solutions having the same consumption of the fresh resource, other objectives should be used (e.g. capital investment, safety, flexibility, operability, etc.).

*Insights on process modifications*

The property-based material-reuse pinch diagram and the aforementioned design rules can be used to guide the engineer in making process modifications to enhance material reuse; for instance, the observation that below the pinch there is deficiency of reusable sources, whereas above the pinch there is a surplus of sources. Therefore, sinks can be moved from below the pinch to above the pinch and sources can be moved from above the pinch to below the pinch to reduce the usage of fresh resources and the discharge of waste. Moving a sink from below the pinch to above the pinch can be

achieved by increasing the upper bound on the property constraint of the sink given by inequality 3.7. Conversely, moving a source from above the pinch to below the pinch can be accomplished by reducing the value of the property operator through changes in operating conditions or by adding an "interception" device (e.g., heat exchanger, separator, reactor, etc.) that can lower the value of the property operator. In such cases, the problem representation shown in Fig. 1 can be extended to account for the addition of new "interception" devices that serve to adjust the properties of the sources. Figure 13 is a schematic representation of the extended problem statement, which incorporates stream allocation, interception, and process modification.

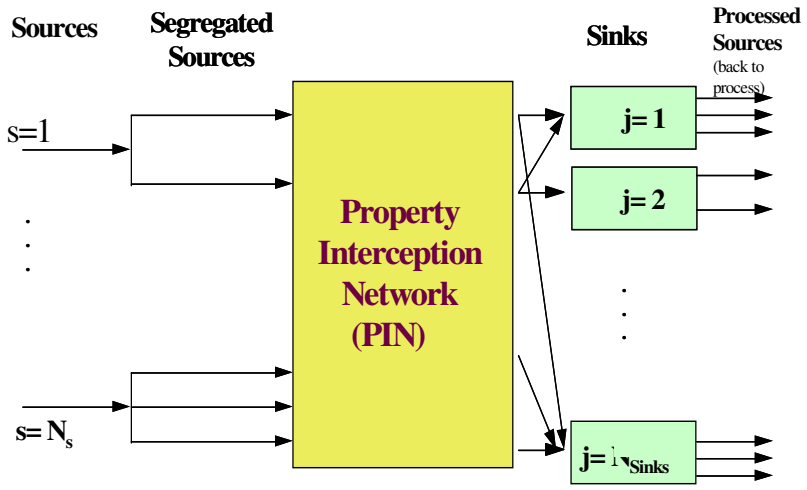


Fig. 13. Schematic representation of property-based allocation and interception.

Figure 14a illustrates an example of the pinch-based representation, when a flowrate, $F_x$ is intercepted and its value of property operator is reduced to match that of the fresh. Compared to the nominal case of Fig. 12, two benefits accrue as a result of this movement across the pinch: both the usage of fresh resource and the discharge of waste are reduced by $F_x$.

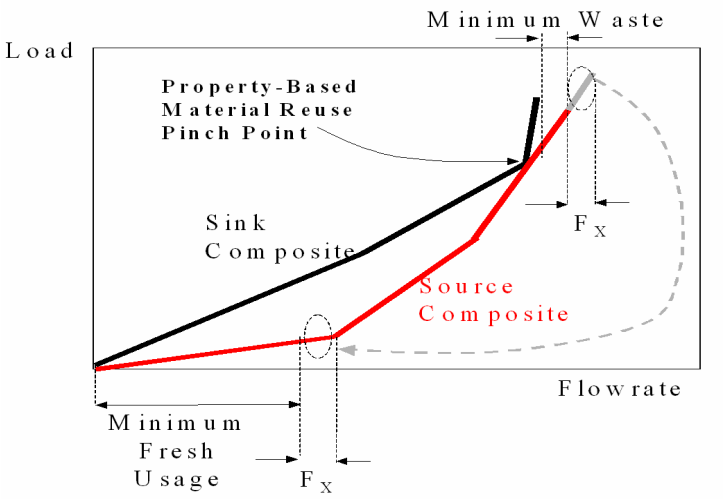


Fig. 14a. Insights for process modification: moving a source across the pinch.

Another alternative is to reduce the load of a source below the pinch (again by altering operating conditions or adding an interception device). Consequently, the cumulative load of the source composite decreases and allows an additional reuse of process sources with the result of decreasing both the fresh consumption and waste discharge. Figure 14b demonstrates the revised pinch diagram for Fig. 12, after the load of the process source (and therefore its slope) below the pinch has been decreased. When slid on the fresh line, an additional amount of the source above the pinch can be reused resulting in a net reduction in fresh and waste.

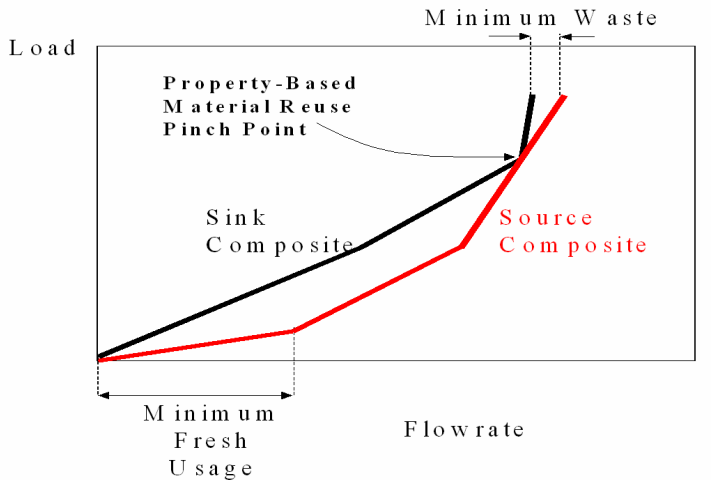


Fig. 14b. Insights for process modification: reducing the load of a source.

## 7. EXTENSION TO OTHER CASES

In the previous analysis, it was assumed that the fresh resource possesses superior properties to all other streams. If that is not the case, then the procedure can be extended by arranging the sources in ascending order of property operators and sliding the source composite stream on the locus of the fresh till the pinch point is obtained by touching the two composites. This procedure is shown in Fig. 15.

Analogously to the aforementioned targeting procedure, we can derive a similar procedure for the case when the fresh resource has the highest value of property operator. In this case, the sink constraint is given by:

$$\psi_j^{\min} \le \psi_j^{in} \le \psi_{Fresh} \tag{3.21}$$

and the minimum property load for a sink is defined as:

$$L_j = G_j * \psi_j^{\min} \tag{3.22}$$

By analogy, in this case the sink and source representations are created in *descending* order of operators starting with the property operator of the fresh (highest slope). The source composite curve is slid on the fresh line pushing it to the left, while keeping it above the sink composite curve, until the two composites touch at the pinch point with

the source composite completely above the sink composite in the overlapped region. The determination of both the minimum consumption of fresh resource and waste discharge is shown in Fig. 16.

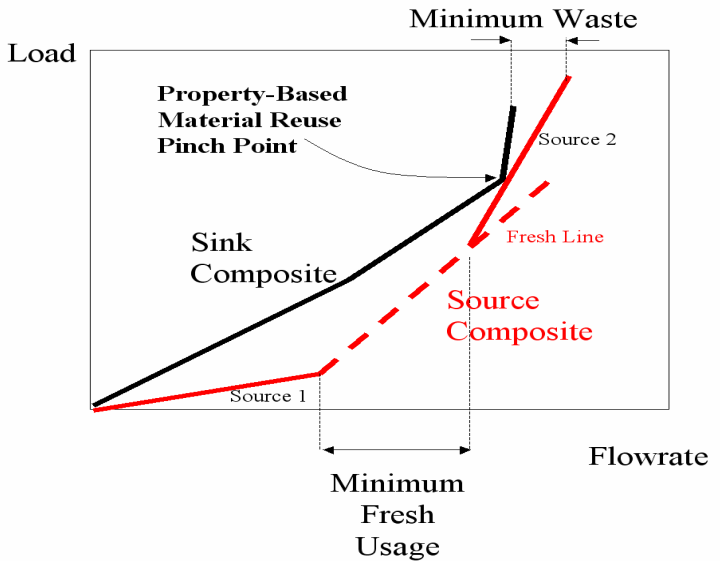


Fig. 15. Property pinch diagram for the case where fresh lies in the middle.

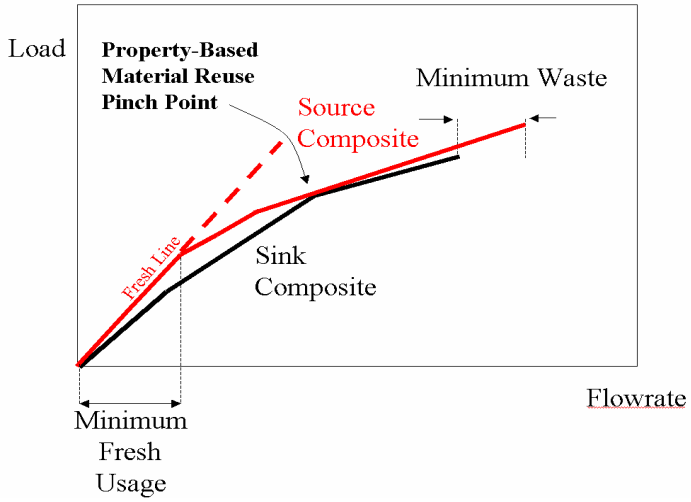


Fig. 16. Property pinch diagram when fresh operator is the upper bound for sink's feasibility.

## 8. RELATIONSHIP TO MASS INTEGRATION AND CONCENTRATION-BASED MATERIAL REUSE PINCH ANALYSIS

Since composition is one class of properties, mass integration can be regarded as a special case of property integration. Indeed, when the property of interest is composition, and the property operator is given by composition, equation 3.2 becomes a component material balance. Thus, the composition-based recycle/reuse problem can be extended to cases, in which fresh resources are not absolutely clean, but they may include a small amount of pollutant. This mass integration problem can be properly tackled in the same manner, as discussed in this work through property integration, in which composition is the property in concern. The case of impure fresh resources then falls into the category of fresh resources with superior properties. Therefore, the property-based pinch analysis presented in this paper is a generalization of the concentration-based material reuse pinch analysis (El-Halwagi et al., 2003).

## 9. CASE STUDIES

Now that the foregoing rules and tools have been developed, we are in a position to proceed to several case studies in order to illustrate the applicability of the developed procedure.

*Case study I: Solvent recycle in metal degreasing*

A metal degreasing process (Shelley and El-Halwagi, 2000) presented in Fig. 17 is considered here. Currently, a fresh organic solvent is used in the degreaser and the absorber. A reactive thermal processing and solvent regeneration system is used to decompose the grease and the organic additives, and regenerate the solvent from the degreaser. The liquid product of the solvent regeneration system is reused in the degreaser, while the gaseous product is passed through a condenser, an absorber and a flare. The process produces two condensate streams: Condensate I from the solvent regeneration unit and Condensate II from the degreaser. The two streams are currently sent to hazardous waste disposal. Since these two streams possess many desirable properties that enable their possible use in the process, it is recommended their

recycle/reuse to be considered. The absorber and the degreaser are the two process sinks. The two process sources satisfy many properties required for the feed of the two sinks.

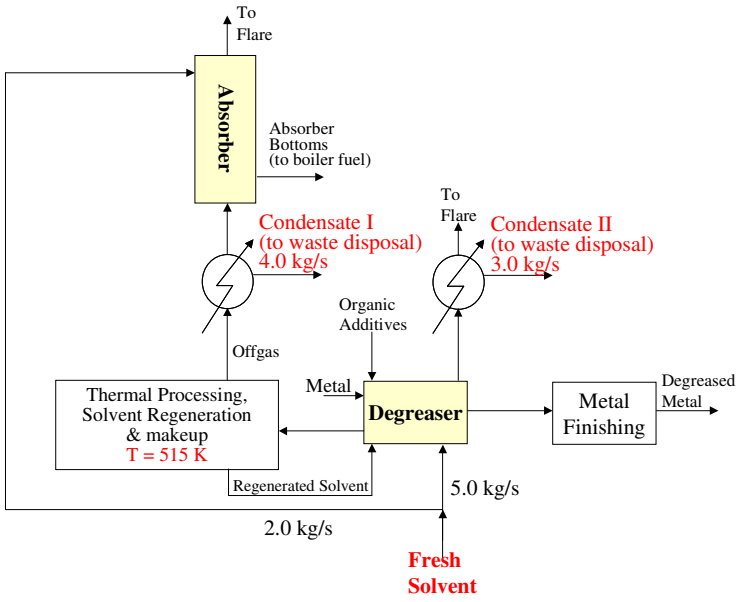


Fig. 17. A degreasing plant.

An additional property should be examined; namely Reid Vapor Pressure (RVP), which is important in characterizing the volatility, makeup and regeneration of the solvent.

The mixing rule for vapor pressure (RVP) is given by the following expression (Shelley and El-Halwagi, 2000):

$$\overline{RVP}^{1.44} = \sum_{i=1}^{N_s} x_i RVP_i^{1.44} \tag{3.23}$$

Moreover, the inlet flowrates of the feed streams to the degreaser and absorber along with their constraints on the property (RVP) are given in Table 2.

Table 2
Flowrates and bounds on properties for sinks – case study 1

| Sink | Flowrate (kg/s) | Lower Bound on RVP (atm) | Upper Bound on RVP (atm) |
|---|---|---|---|
| Degreaser | 5.0 | 2.0 | 3.0 |
| Absorber | 2.0 | 2.0 | 4.0 |

The RVP for Condensate I is a function of the thermal regeneration temperature as follows:

$$\mathrm{RVP}_{\text{Condensate I}} = 0.56e^{\left(\frac{T-100}{175}\right)} \qquad (3.24)$$

where $\mathrm{RVP}_{\text{Condensate I}}$ is the RVP of condensate I in atm and T is the temperature of the thermal processing system in K. The acceptable range of this temperature is 430 to 520 K. At present, the thermal processing system operates at 515 K leading to an RVP of 6.0. The data for Condensate I and Condensate II are given in Table 3.

Table 3
Properties of process sources and fresh – case study 1

| Source | Flowrate (kg/s) | RVP (atm) |
|---|---|---|
| Process Condensate I | 4.0 | 6.0 |
| Process Condensate II | 3.0 | 2.5 |
| Fresh Solvent | To be determined | 2.0 |

After gathering the data, the aforementioned targeting procedure is followed. First, we convert the property values to operator values by considering the mixing rule for vapor pressure (equation 3.23). Then, since the operator of the fresh is less than those of the sources, we evaluate the maximum admissible property loads ($U_j$ ) for sinks 1 and 2 using equation 3.12. Next, we construct the sink and source composite curves in ascending order of operators and slide the source composite on the fresh line until the two composites touch at the pinch point, as shown in Fig.18. Thus, we can graphically

determine the fresh consumption, which is 2.38 kg/s and the waste discharge, which is 2.38 kg/s as well. The fresh solvent consumption is, therefore, reduced by 66%. This target is identified through direct recycle/reuse.

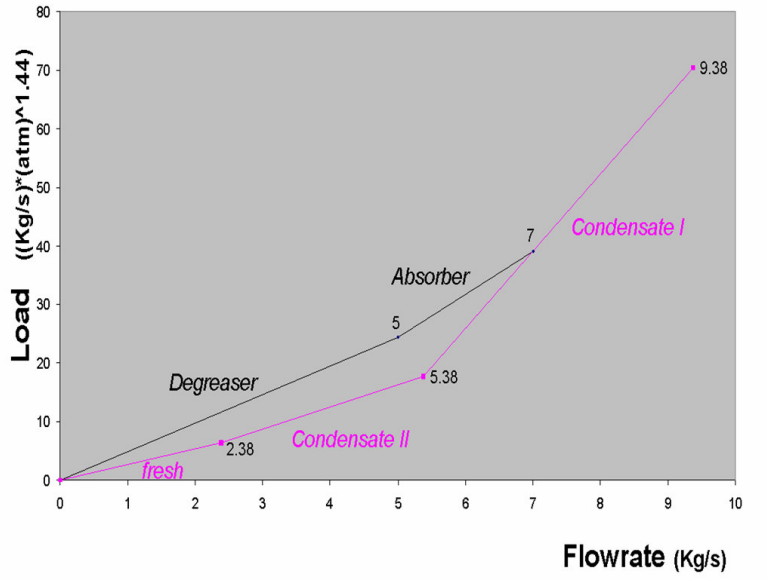


Fig. 18. Property-based pinch diagram for the degreasing case study.

As mentioned earlier, reuse can be enhanced through process modifications. For instance, if it is desired to completely eliminate the fresh consumption by reducing the load of Condensate I, a net reduction of 26.59 kg*atm$^{1.44}$/s is required. This is equivalent to reducing the RVP of Condensate I to 3.688 atm. According to equation 3.24, in order to achieve this RVP, the temperature of the thermal processing system should be reduced to 430 K. Fig. 19 shows the property-based pinch diagram after reducing the RVP of Condensate I, where the pinch location has now changed. Following the matching approach illustrated in Fig. 9, we can assign the sources to sinks and develop the solution, which satisfies the new target (no fresh), as shown by Fig. 20.

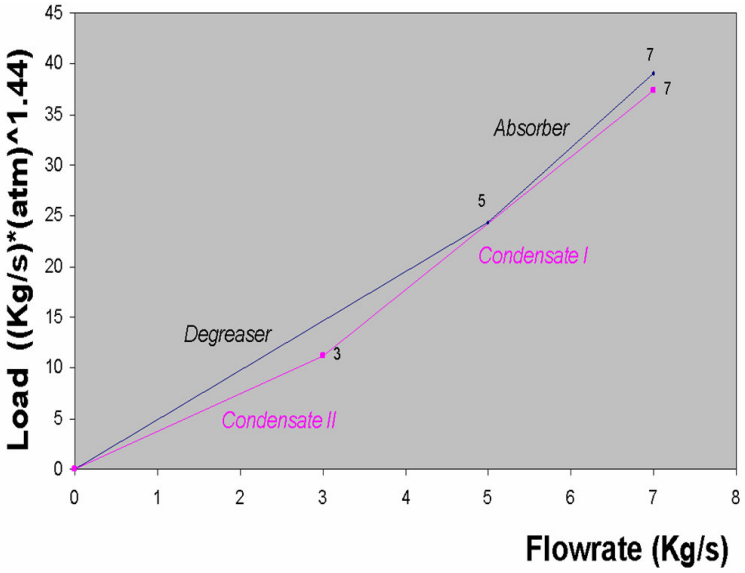


Fig. 19. Property-based pinch diagram after process modification.

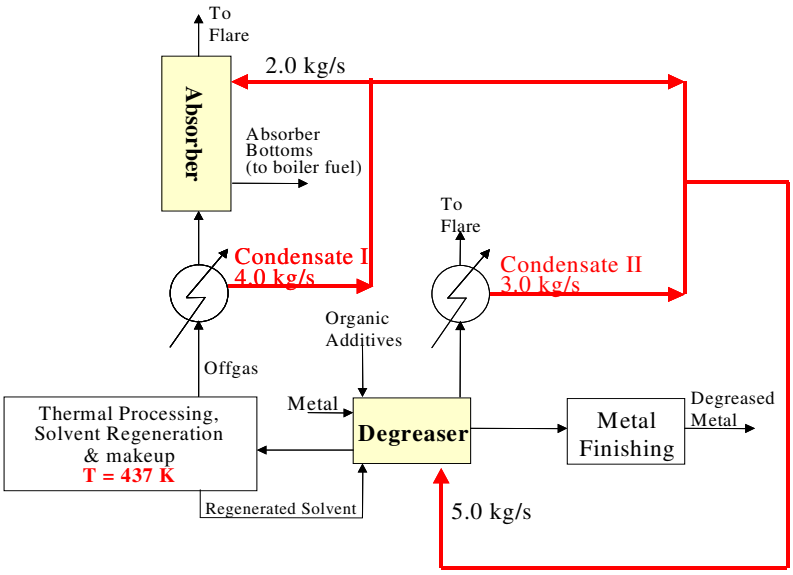


Fig. 20. Solution to the degreasing case study with process changes and source reuse.

*Case study II: Water reuse in microelectronic process*

A case study of a microelectronic manufacturing facility is presented here (Zant, 1997; Wu et al., 2004). The assembly process in the manufacturing of semiconductors

consumes a large amount of high-purity water (HPW), which results in generating a large amount of wastewater, as well. Fig. 21 shows a general flowsheet, where the Wafer Grinding (Backgrinding) and the Marking processes are identified as the sinks of the problem that both accept high-purity water as their feed. In particular, the wafer backgrinding process requires water of higher purity, whereas the plating and marking processes have looser constraints on the purity of their feed.

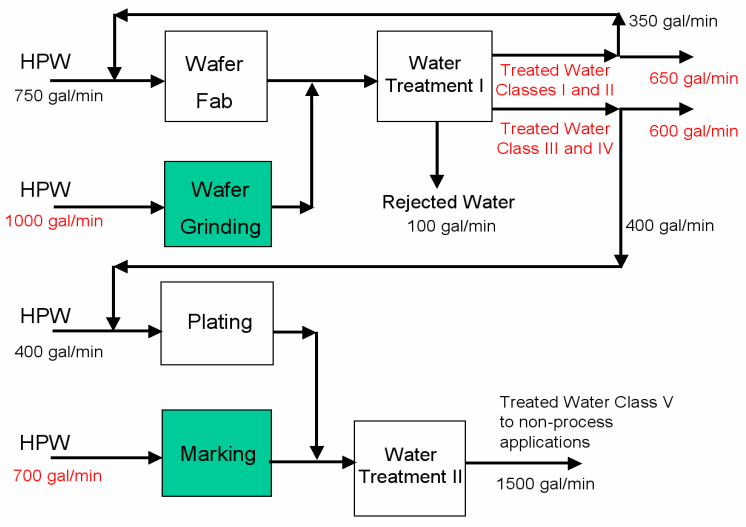


Fig. 21. A microelectronics manufacturing flowsheet.

HPW can be classified into four categories (Zant, 1997; Wu et al., 2004): classes I and II are defined as high grade HPW, which can be recycled to wafer-related processes, such as wafer etching, backgrinding, sawing, etc. Classes III and IV are low grade HPW, which can be consumed by integrated circuits (IC)–related processes, such as marking, electroplating, singulation, etc. In addition, the reclaimed water from the plating and marking processes can only be used in non-process applications, such as cooling towers, scrubbers, etc.

Thus, in the present process there are two main process sources that are available for reuse to the sinks; namely the treated water streams of two different grades (classes I-II

and classes III – IV). Part of the treated water of classes I and II is already recycled to a wafer fabrication unit, and part of the treated water of classes III and IV is reused in the plating process. We are interested in reusing the remaining flowrate of the process sources, which is 1250 gal/min in total, as feed to the sinks, in order to reduce the HPW consumption. The main characteristic that we consider here, in order to evaluate the reuse of the treated streams to the sinks, is resistivity (R), which constitutes an index of the ionic content of aqueous streams.

The mixing rule for resistivity is the following (Gabriel et al., 2003):

$$\frac{1}{\overline{R}} = \sum_{i=1}^{N_s} \frac{x_i}{R_i} \tag{3.25}$$

Moreover, the inlet flowrates of the feed streams to the Backgrinding and Marketing processes, along with their constraints on resistivity are given in Table 4, whereas the source flowrates and property values are given in Table 5.

Table 4
Flowrates and bounds on properties for sinks – case study 2

| Sink | Flowrate (gal/min) | Lower Bound on R (kΩ*cm) | Upper Bound on R (kΩ*cm) |
|---|---|---|---|
| Backgrinding | 1000 | 16000 | 18000 |
| Marking | 700 | 10000 | 18000 |

Table 5
Properties of process sources and fresh – case study 2

| Source | Flowrate (gal/min) | R (kΩ*cm) |
|---|---|---|
| Water of Class I-II | 650 | 14,000 |
| Water of Class III-IV | 600 | 12,000 |
| HPW (fresh) | To be determined | 18,000 |

Next, we construct the composite curves in ascending order of operators starting with the fresh (Fig. 22). Based on the pinch diagram, we can determine the target for minimum usage of fresh consumption for the whole process, which is 562.516 gal/min

and the minimum waste discharge, which is 112.516 gal/min. The reduction in HPW usage is almost 49%.

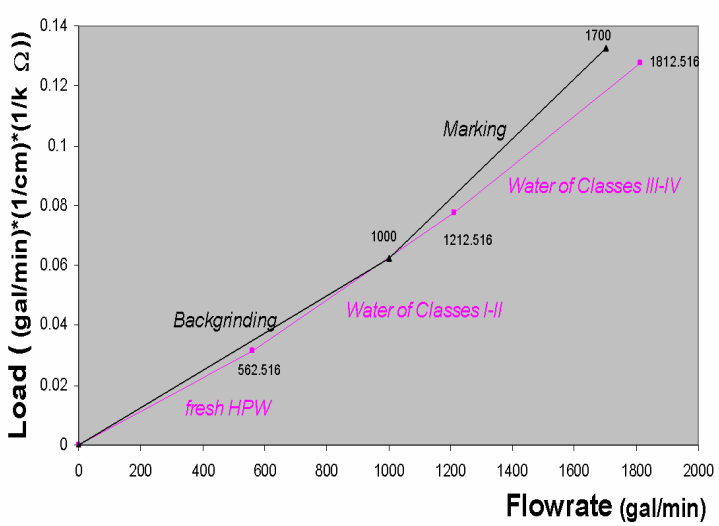


Fig. 22. Source and sink composite curves for the microelectronics facility case study.

*Case study III: Waste fiber recycle in papermaking process*

A papermaking process is presented in this case study (El-Halwagi et al., 2004). Fig. 23 indicates that two different paper machines (paper machines I and II) are regarded as sinks and demand a certain amount of fiber (bleached pulp). An external fresh source is also available to be purchased and used to paper machine II in order to supplement the need for fiber feed to the sinks. The objective of this case study is to explore the possibilities of recycling and reusing the waste fiber streams (broke) that were rejected as a result of processing failing and interruptions, thus reducing the fresh fiber consumption and maximizing the resource usage.

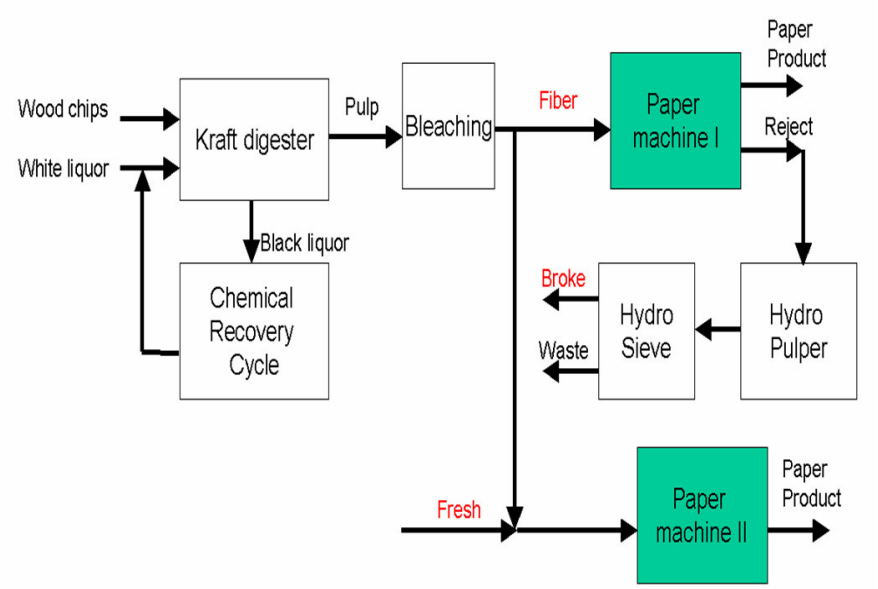


Fig. 23. A papermaking manufacturing flowsheet (El-Halwagi et al., 2004).

To evaluate the quality of the broke to be used as a feed stream to the sinks, we focus on reflectivity, which is a key property for the produced paper. It is defined as the reflectance of an infinitely thick material compared to an absolute standard, which is magnesium oxide.

The mixing rule for reflectivity $R_\infty$ is of the following form (El-Halwagi et al., 2004):

$$\overline{R}_{\infty}^{5.92} = \sum_{i=1}^{N_s} x_i R_{\infty_i}^{5.92} \qquad (3.26)$$

Tables 6 and 7 provide the data for the property constraints of the sinks and the properties of the process sources and the fresh, along with their flowrates.

Table 6
Flowrates and bounds on properties for sinks – case study 3

| Sink | Flowrate (ton/hr) | Lower Bound on $R_\infty$ | Upper Bound on $R_\infty$ |
|---|---|---|---|
| Paper Machine I | 100 | 0.85 | 0.95 |
| Paper Machine II | 40 | 0.90 | 0.95 |

Table 7
Properties and flowrates of fiber sources – case study 3

| Source | $R_\infty$ | Flowrate (ton/hr) |
|---|---|---|
| Process Fiber | 0.88 | 90 |
| Broke | 0.75 | 60 |
| External (Fresh) Fiber | 0.95 | To be determined |

After gathering all the data shown in Tables 6 and 7, we can follow the procedure for the case where fresh has the highest operator value. Therefore, we can create the source and sink composite curves in descending order of operators for both the sinks and sources, as shown in Fig. 24. From Fig. 24 we can directly identify the minimum fresh and waste discharge targets, and conclude that instead of using 50 ton/hr of fresh fiber, we can only use 14.95 ton/hr, whereas the waste discharge is 24.95 ton/hr. Thus, we achieve a reduction in fresh usage of about 70%.

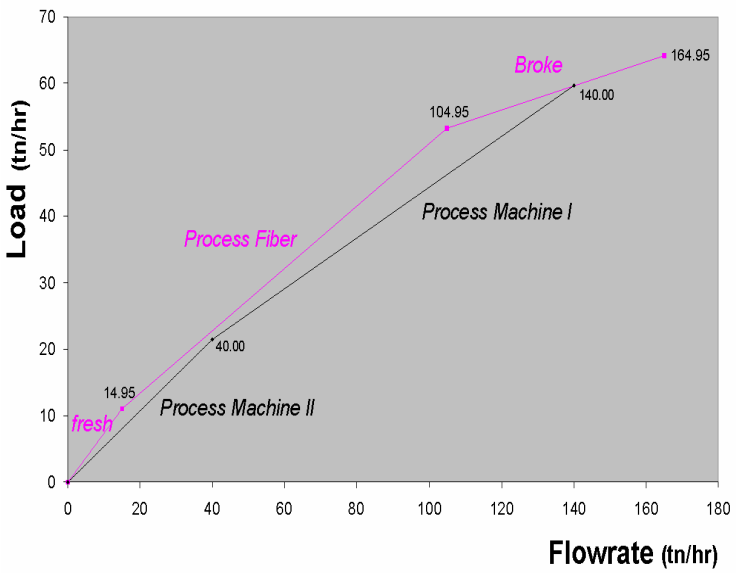


Fig. 24. Source and sink composite curves for the papermaking case study.

# CHAPTER IV
# ALGEBRAIC TECHNIQUE FOR TARGETING MATERIAL REUSE THROUGH PROPERTY INTEGRATION

## 1. INTRODUCTION

Although the graphical technique, which was discussed in the previous chapter, provides key visualization insights for targeting and network synthesis, it is essential to develop a systematic algebraic procedure, which is particularly useful in the following cases:

- Problem dimensionality: As the number of sources and sinks increases, it becomes more convenient to use spreadsheets or algebraic calculations to handle the targeting.
- Scaling problems: If there is a significant difference in values of flowrates and/or property loads for some of the sources and/or sinks, or when the property operators and loads of process sources or sinks are of different magnitudes, the graphical representation becomes inaccurate, since the larger flows/loads will skew the scale for the other streams.
- Computational effectiveness: If the targeting is tied with a broader design task that is handled through algebraic computations, it is desirable to use consistent algebraic tools for all the tasks. Thus, the algebraic procedures can be easily automated and coded to enhance computational effectiveness. For instance, in sensitivity analysis, the algebraic technique can be readily used to estimate the solution sensitivity to variations in input data by running what-if scenarios. Graphical procedures are cumbersome in sensitivity analysis, since they may entail the re-plotting of the composite curves for each variation.
- Interaction with process simulators: The algebraic procedure is naturally implemented on a spreadsheet. Many computer-aided process simulation tools are interactive with spreadsheets. Hence, the property information can be

automatically extracted from the simulation and the targeted results from the spreadsheet are fed back to the simulator.

Therefore, this chapter introduces a new property-based, non-iterative and systematic algebraic procedure to the targeting of property-based material recycle networks. The problem involves the allocation of process streams and fresh sources to process units (sinks) with the objective of minimizing fresh usage and waste discharge. Property constraints dictated by the property-driven problem requirements and characteristics govern the allocation of streams to processing units. First, observations from the graphical targeting approach, which was described in the previous chapter, are transformed into algebraic insights. Then, a geometrical transformation is developed to account for the property operators of fresh resources. These insights and geometrical transformations lead to the development of a property-based cascade analysis, which identifies and adjusts any material recycle infeasibilities in order to maximize the recycle opportunities. The developed procedure also identifies the location of the property-based material recycle pinch point and demonstrates its significance in managing process sources, fresh usage, and waste discharge. In addition, the algebraic approach directly identifies rigorous targets for minimum usage of fresh resources, maximum recycle of process sources to process units, and minimum discharge of waste. Two case studies are solved to illustrate the ease, rigor, and applicability of the developed targeting technique, and its relationships to the property-based material recycle pinch analysis.

Some of the advantages of the developed methodology include its simplicity, the ability to deal with any resource conservation operations, the possibility of determining all possible network configurations that correspond to the absolute fresh and waste material targets, and finally the capability of being embedded in an overall process design scheme and program.

## 2. PROBLEM STATEMENT

The problem definition of a property-based material reuse network is the following:

Given is a process with a number ( $N_{sources}$ ) of process sources (process streams and waste) that can be considered for possible reuse and replacement of the fresh material. Each source, $i$ , has a flowrate of $F_i$, and a property value of $p_i$ ($i$ = 1, 2, …., $N_{sources}$).

A number ( $N_{sinks}$ ) of process units (sinks), is also considered. Each sink $j$ can accommodate a feed of given flowrate $G_j$ , with an inlet property value, $p_j^{in}$ that lies within predefined upper and lower bounds, e.g.

$$p_j^{\min} \le p_j^{in} \le p_j^{\max} \quad , \; j = 1,2,\text{K} \; , N_{sinks} \; . \tag{4.1}$$

A fresh (external) resource, with a property value of $p_{Fresh}$ that can be purchased to supplement the use of process sources in sinks, is also available.

The objective is to develop a systematic, non-iterative property-based algebraic procedure aiming at minimizing the purchase of fresh resource, maximizing the usage of process sources, and minimizing waste discharge.

## 3. ALGEBRAIC CONDITIONS FOR FEASIBILITY

First, let us consider the graphical representations of the source and sink composites, as discussed and described in the previous chapter. For now, only the process sources and the sinks are represented, and the resulting infeasibilities are to be examined (Fig. 25). Feasibility conditions dictate that at any given flowrate, the admissible property load to sinks must be greater than or equal to that of the sources.

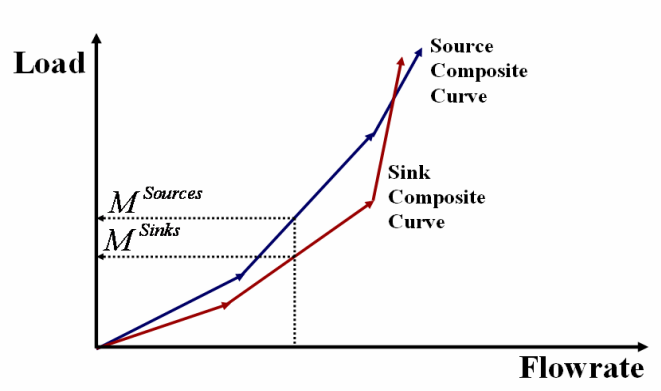


Fig. 25. Infeasibility in property loads.

On the other hand, looking horizontally (at any given load), the flowrate of the sources must be greater or equal to that of the sinks (Fig. 26). Otherwise, if source composite lies to the left of sink composite, this leads again to infeasibility (shortage in flowrate).

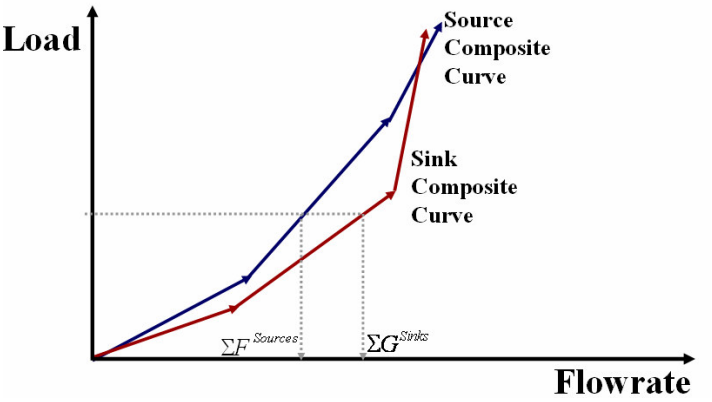


Fig. 26. Infeasibility in flowrates (shortage).

Since each composite represents a piecewise linear function, the maximum infeasibility will be at the corner points. Therefore, let us draw horizontal lines at the corner points of the source and sink composites as shown in Fig. 27. These horizontal

lines are numbered using an index $k$, which starts with $k = 0$ at the zero property load level and are numbered in ascending order. The load at each horizontal level, $k$, is referred to as $M_k$.

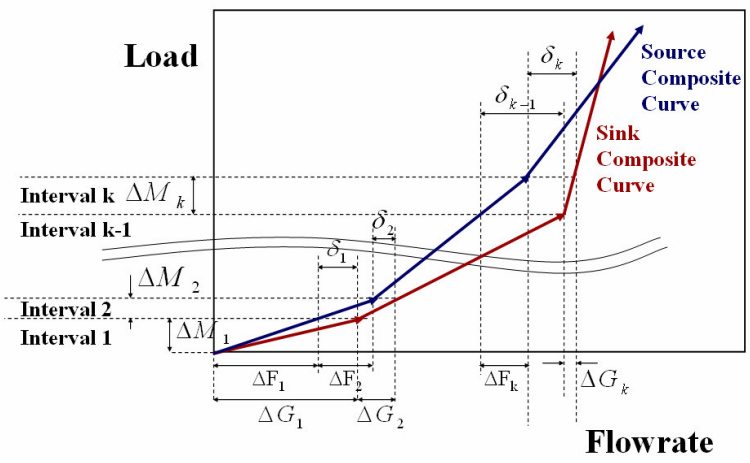


Fig. 27. Property load intervals, flowrates, and property residuals.

Next, we define $M_k$ as the difference between the property load of the source or the sink and the property load of a fresh stream. Therefore, we calculate the loads of the sink and the source as follows:

$$M_j^{Sink,\max} = G_j(\psi_j^{\max} - \psi_{Fresh}) = G_j \Psi_j^{\max} \tag{4.2}$$

where $\Psi_j^{\max} = \psi_j^{\max} - \psi_{Fresh}$ (4.3)

and

$$M_i^{Source} = F_i(\psi_i - \psi_{Fresh}) = F_i \Psi_i \tag{4.4}$$

where $\Psi_i = \psi_i - \psi_{Fresh}$ (4.5)

Next, the vertical distance between each two horizontal lines is referred to as the *property load interval* and is given the index $k$, as well. The load within interval $k$ is calculated as follows:

$$\Delta M_k = M_k - M_{k-1} \tag{4.6}$$

The flowrates of the source and the sink within interval $k$ correspond to the horizontal distances on the source/sink composite curves enclosed within the interval. Hence, they can be calculated as follows:

$$\Delta F_k = \frac{\Delta M_k}{\psi_{\text{source in interval k}}} \tag{4.7}$$

and

$$\Delta G_k = \frac{\Delta M_k}{\psi^{\max}_{\text{sink in interval k}}} \tag{4.8}$$

As with the mass integration algebraic technique (Almutlaq and El-Halwagi, 2005), it can be proved that at any interval $k$ with property load $M_k$ and property load interval $\Delta M_k$, we can obtain:

$$F_k^{Sources} = \frac{\Delta M_k}{\psi_{\text{source in interval k}}} + \sum_{n=1}^{k-1} \Delta F_n = \sum_{n=1}^{k} \Delta F_n \tag{4.9}$$

where $F_k^{Sources}$ is the total flowrate of the sources that is available for use to the sinks up to interval $k$.

$$F_k^{Sinks} = \frac{\Delta M_k}{\psi^{\max}_{\text{sink in interval k}}} + \sum_{n=1}^{k-1} \Delta G_n = \sum_{n=1}^{k} \Delta G_n \tag{4.10}$$

where $F_k^{Sink}$ is the total flowrate required by the sinks up to interval $k$.

For feasibility to be attained in the $k^{th}$ interval, there exists $\delta_k^{'}$ such that

$$F_k^{Sources} + \delta_k^{'} \geq F_k^{Sink} \tag{4.11}$$

where $\delta_k^{'} \geq 0$ is the amount of the flowrate needed to eliminate any infeasibilities caused by the difference between the flowrate of the sources and the required flowrate of the sinks in interval k.

## 4. DERIVING THE CASCADING PROCEDURE

As seen in Fig. 27, for any given property load the sink composite curve must lie to the left of the source composite curve. In this way, there will not be any shortage of the

flowrate that is required by the sinks, as described in the feasibility conditions stated above. The most negative number of all δ's (which is designated as $\delta_{max}$) constitutes the maximum shortage of flowrate and corresponds to the minimum usage of fresh source. By sliding the source composite curve onto the fresh locus to the right by a distance equal to $\delta_{max}$, as shown in Fig. 28, we eliminate all infeasibilities. Consequently, the target for minimum fresh usage is equal to the maximum shortage, i.e.

$$\text{Target for Minimum Fresh Consumption} = \left|\delta_{max}\right| = \delta_0' \qquad (4.12)$$

where $\delta_0'$ indicates the total minimum amount of flowrate needed to eliminate all infeasibilities in the process. This flowrate can be added to the first interval to yield feasible material balances around all remaining intervals.

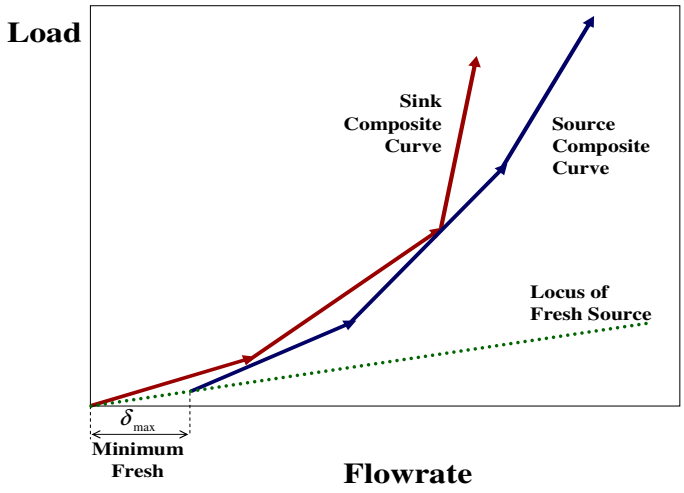


Fig. 28. Minimum fresh target corresponds to maximum flowrate shortage.

In order to develop the algebraic procedure, it is necessary to evaluate this maximum flowrate shortage algebraically. Towards this end, the feasibility conditions stated above will be utilized by changing the inequalities of flowrates into equalities for each interval,

i.e. equation 4.11 can be written as:

$$F_k^{Sources} + \delta_k = F_k^{Sinks} \tag{4.13}$$

We define a positive $\delta_k$ as a surplus and a negative $\delta_k$ as a deficit (corresponding to infeasibility). Substituting equations 4.9 and 4.10 into equation 4.13 and re-arranging, we get:

$$\delta_k = \sum_{n=1}^{k} \Delta F_n - \sum_{n=1}^{k} \Delta G_n \tag{4.14}$$

Moreover, for the $k^{th}$ interval, we have:

$$\delta_k = \delta_{k-1} + \Delta F_k - \Delta G_k \tag{4.15}$$

with $\delta_0 = 0$. Equation (4.15), which represents the flowrate balance within a property load interval $k^{th}$, is illustrated in Fig. 29.

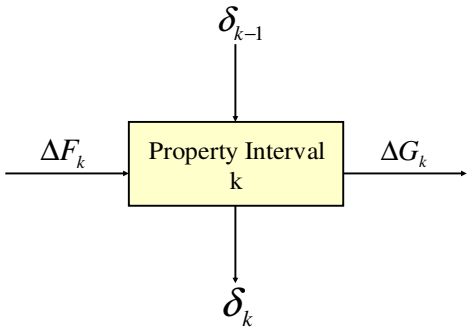


Fig. 29. Flowrate balance around a property load interval.

The flowrate balances can be carried out for all property intervals resulting in the cascade diagram shown in Fig. 30a. In the cascade diagram, the most negative value of $\delta$ (referred to as $\delta_{\max}$) corresponds to the target for minimum fresh consumption as indicated by equation 4.12 and the amount of waste is equal to the sum of $\delta_{\bar{k}}$ and $|\delta_{\max}|$. Next, in order to remove the infeasibilities, a flowrate of the fresh resource of $|\delta_{\max}|$ is added to the top of the cascade (i.e., $\delta_0' = |\delta_{\max}|$) and the residuals of all intervals are

adjusted, thus eliminating all the infeasibilities. The result is that the most negative residual now becomes zero indicating the property-based pinch location. The property-based pinch location corresponds to the highest point, at which the cumulative flows of the sources equal those of the sinks and the cumulative property loads of the sources equal the maximum allowed by the sinks. Furthermore, the revised residual leaving the last interval is the target for minimum waste discharge. These results are shown on the revised cascade diagram illustrated in Fig. 30b.

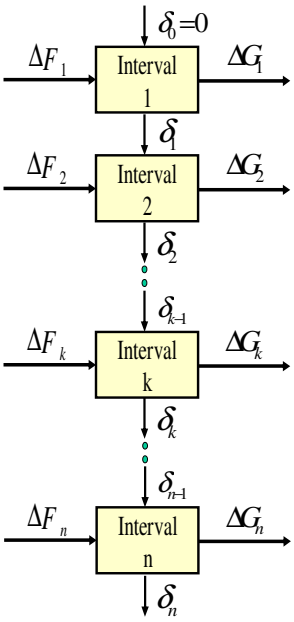


Fig. 30a. Infeasible property-based cascade diagram.

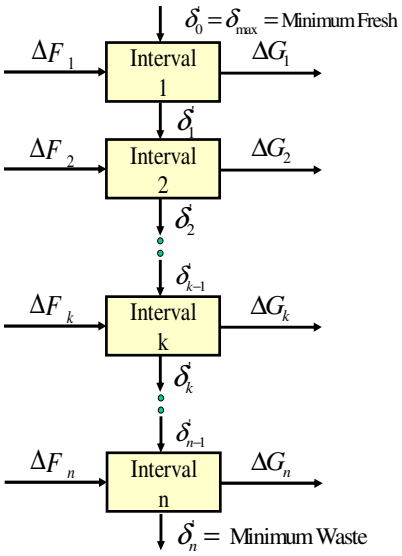


Fig. 30b. Revised property-based cascade diagram.

## 5. ALGEBRAIC TARGETING PROCEDURE FOR PROPERTY-BASED APPLICATIONS

In developing the algebraic targeting procedure for property-based systems, we first need to revise the technique described in the previous paragraph by accounting for the property load change that is caused by the non-zero value of the property of the fresh for the general case. To develop the algebraic procedure for the case shown in Fig. 28, the following techniques are suggested:

1. The coordinate system can be changed by rotating the flowrate-axis anti-clockwise by a degree $(\theta)$, so that it coincides with the fresh feed locus, as shown in Fig. 31, where

$$\theta = \tan^{-1} \psi_{Fresh} \tag{4.16}$$

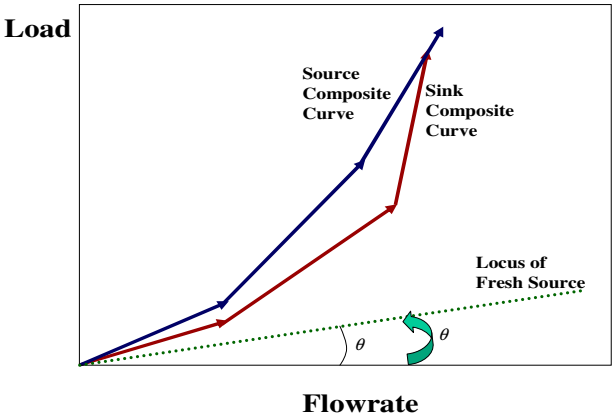


Fig. 31. Rotation of composite curves by the angle of fresh resources locus.

Towards this end, we need to account for a respective change in the flowrates and property operators for all the components of the system, according to Fig. 31. The changes in the variables are described by the following expressions:

$$G_j^{'} = G_j \cos\theta \tag{4.17}$$

and

$$F_i^{'} = F_i \cos\theta \tag{4.18}$$

Then, the new property operators can now be expressed as in equations 4.3 and 4.5, i.e.:

$$\Psi_j^{\max} = \psi_j^{\max} - \psi_{Fresh} \tag{4.3}$$

$$\Psi_i = \psi_i - \psi_{Fresh} \tag{4.5}$$

In addition, the corresponding loads for sinks and sources are:

$$M_j^{'} = G_j^{'}\Psi_j^{\max} \tag{4.19}$$

$$M_i^{'} = F_i^{'}\Psi_i \tag{4.20}$$

The target for minimum fresh source consumption and waste discharge are brought back to the old coordinate system through the following expressions:

$$\text{Target for Minimum Fresh Consumption } = \delta_0^{'} / \cos(\theta)$$

and

$$\text{Target for Minimum Waste Discharge } = \delta_n^{'} / \cos(\theta)$$

The same outcome is obtained by rotating the system clockwise, so as the fresh locus coincides with the flowrate-axis of the new coordinate system.

2. An alternate method involves the adjustment of the property load contribution of the fresh feed on both composites, as shown in Fig. 32. The load contribution of the fresh is the product of its flowrate and property operator and, therefore, may be readily calculated. In this case, the residuals (including $\delta_{\max}$ or the target for minimum fresh consumption) may be calculated by first determining $\Delta F_k$ and $\Delta G_k$ for any interval $k$, and then calculating the residuals based on the property interval balances. The goal is to generate an equation that eliminates the use of the fresh flowrate and/or the fresh property load, since these are the unknown variables in the problem.

According to equation 4.7 and Fig. 32, $\Delta M_k^{tot}$ may be regarded as the total property load within interval $k$, which incorporates both the load of the source and the load of the fresh in interval $k$. Thus, $\Delta F_k$ is given by:

$$\Delta F_k = \Delta M_k^{tot} / \psi_{i,k} = (M_k^{tot} - M_{k-1}^{tot}) / \psi_{i,k} \tag{4.21}$$

or

$$\Delta F_k = [(M_k + M_{fr,k}) - (M_{k-1} + M_{fr,k-1})] / \psi_{i,k}$$

or

$$\Delta F_k = (M_k - M_{k-1}) / \psi_{i,k} + (M_{fr,k} - M_{fr,k-1})] / \psi_{i,k} \tag{4.22}$$

where $M_k$ and $M_{k-1}$ are now the property loads contributed purely from the source in intervals $k$ and $k-1$ respectively, whereas $M_{fr,k}$ and $M_{fr,k-1}$ are the property loads of the fresh in intervals $k$ and $k-1$ respectively, as seen in Fig. 32.

In Fig. 32, one can also observe that the source flowrate within interval k, $\Delta F_k$ can be related to the property load of the fresh within this interval, i.e.

$$\Delta F_k = \Delta M_{fr} / \psi_{fr} = (M_{fr,k} - M_{fr,k-1}) / \psi_{Fresh} \tag{4.23}$$

Thus, combining equations 4.22 and 4.23, the following equation can be obtained:

$$\Delta F_k = (M_k - M_{k-1}) / \psi_{i,k} + \Delta F_k \psi_{Fresh} / \psi_{i,k} \tag{4.24}$$

or after rearranging:

$$\Delta F_k = (M_k - M_{k-1}) / (\psi_{i,k} - \psi_{Fresh}) = \Delta M_k / (\psi_{i,k} - \psi_{Fresh}) \tag{4.25}$$

Similarly, $\Delta G_k$ is given by:

$$\Delta G_k = \Delta M_k / (\psi_{j,k}^{\max} - \psi_{Fresh}) \tag{4.26}$$

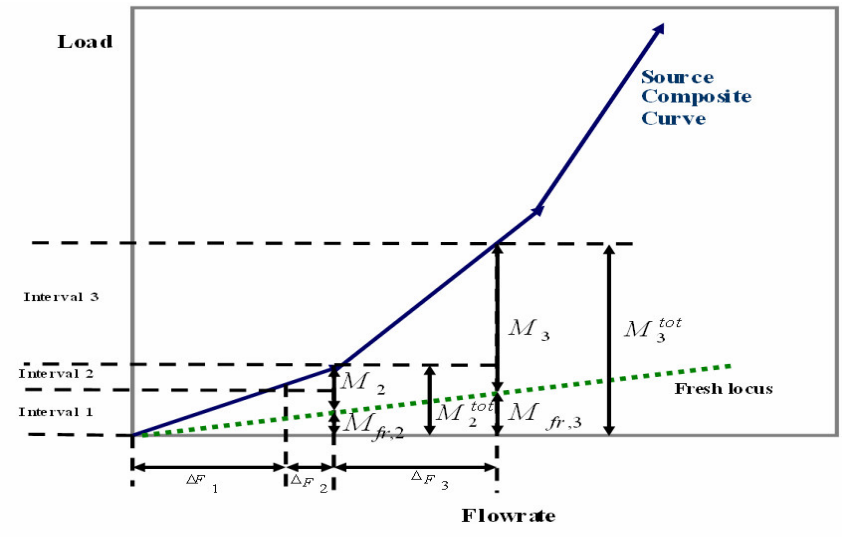


Fig. 32: Elimination of fresh source contribution from the source composite curve.

Another issue in the property-based algebraic calculations for material recycle/reuse is the presence of a process source with a property operator that is less than the operator of the fresh source, as shown in Fig. 33. In such a case, the source prioritization rule is applied to every process source with property operator less than the one of the fresh source prior to applying the method, thus splitting the problem into two sub-problems; one before the introduction of fresh sources and one after.

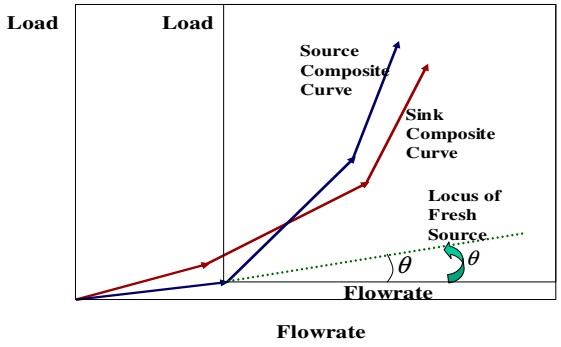


Fig. 33: Case with property operator of process source less than the fresh source operator.

Based on the foregoing analysis, the algebraic procedure for property-based material recycle/reuse problems can be summarized as follows:

1. Rank the sinks in ascending order of maximum admissible property operator, $\psi_1^{\max} \le \psi_2^{\max} \le ...\psi_j^{\max} ... \le \psi_{N_{Sinks}}^{\max}$
2. Rank sources in ascending order of property operators, i.e. $\psi_1 \le \psi_2 \le ...\psi_i ... \le \psi_{N_{Sources}}$
3. If necessary, apply the source prioritization rule for all sources $i$, whose property operators are $\psi_i \le \psi_{Fresh}$ and eliminate them from the ranking, as well as for all sinks with flowrates that have been satisfied by those eliminated sources, such that

   $$\sum_{i=1}^{N_{Sources}} F_i - \sum_{j=1}^{N_{Sinks}} G_j = 0 \qquad \forall i : \psi_i \le \psi_{Fresh}$$

4. Next, eliminate the fresh source property load contribution by subtracting the property operator of the fresh from that of sources and sinks as follows:

   $$\Psi_i = \psi_i - \psi_{Fresh}$$

   $$\Psi_j^{\max} = \psi_j^{\max} - \psi_{Fresh}$$

5. Calculate the property load of each sink ($M_j^{Sink,\max} = G_j \Psi_j^{\max}$) and source ($M_i^{Source} = F_i \Psi_i$).
6. Compute the cumulative property loads for the sinks and for the sources (by summing up their individual property loads).
7. Rank the cumulative property loads in ascending order.
8. Develop the property load-interval diagram (PLID) shown in Fig. 34. First, the property loads are represented in ascending order. The scale is irrelevant. Next, each source (and each sink) is represented as an arrow whose tail corresponds to its starting property load and head corresponds to its ending property load. Equations 4.2-4.8 are used to calculate the intervals property loads, source

flowrates, and sink flowrates.

9. Based on the interval source- and sink- flowrates, develop the property cascade diagram and carry out flowrate balances around the intervals to calculate the values of the flowrate residuals ($\delta_k$'s). The most negative $\delta_k$ is the target for minimum fresh consumption.
10. Revise the property cascade diagram by adding the maximum $|\delta_{\max}|$ to the first interval and calculate the revised residuals. The residual flowrate leaving the last interval is the target for minimum waste discharge. The interval with the first zero residual is the property-based material recycle/reuse global pinch point.

As with the graphical technique, it worth mentioning here that in case fresh has the highest property operator value, the algebraic method holds again in the same manner, except for the ranking part that needs to be carried out in descending order of property operators. Unlike the general case we examined previously, fresh feed in property integration problems is not always available at the highest (or "superior") operator level. That has an effect on how the limiting data is extracted for a case study. As it is shown later in the second case study of this chapter, the lower liming loads (lower bounds of the sink constraints) need to be taken into account, and these are the ones who define the design solution.

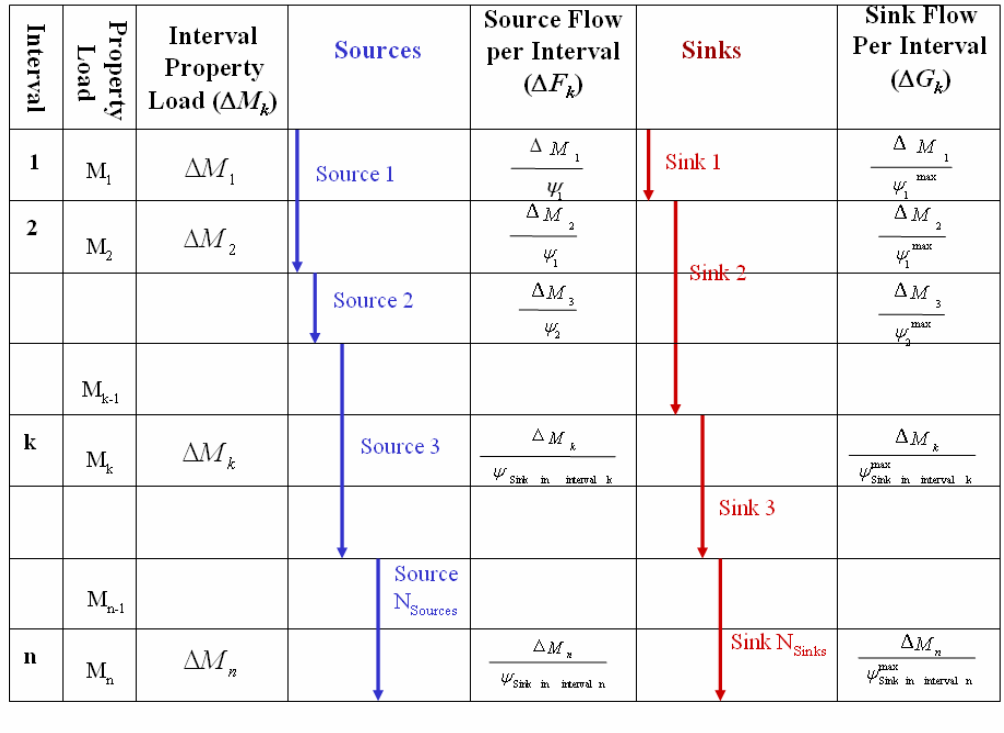


Fig. 34: Property Load Interval Diagram (PLID).

## 6. CASE STUDIES

*Case study I: Solvent recycle in metal degreasing*

The case study of the metal degreasing process presented in the previous chapter is revisited here (Fig. 17). Two available sinks and two process sources can be identified for possible recycle/reuse. Flowrate and vapor pressure values and constraints pertaining to the elements of this process system are shown in Table 8.

Based on this information, the algebraic procedure developed and described previously can be followed, and pertinent calculations on the property loads, flowrates and cumulative loads need to be carried out. It is worth emphasizing again that the property load contribution of the fresh needs to be eliminating, by subtracting the property operator value of the fresh from that of sources and sinks. After these

calculations, the property load interval diagram (PLID) can be constructed and is shown in Fig. 35.

Table 8
Metal degreasing case study information

| Sink | Flowrate, kg/s | RVP, psi | Operator Ψ=RVP^1.44 | Cum. Mass Flow, kg/s | Cum. Mass Load, kg/s |
|---|---|---|---|---|---|
| Degreaser | 5 | 3 | 4.86 | 5 | 24 |
| Absorber | 2 | 4 | 7.36 | 7 | 39 |
| **Sources** | **Flowrate kg/s** | **RVP, psi** | **Operator Ψ=RVP^1.44** | **Cum. Mass Flow, kg/s** | **Cum. Mass Load, kg/s** |
| Fresh | To be determined | 2 | 2.71 | | |
| Condensate II | 3 | 2.5 | 3.74 | 5.3816616 | 18 |
| Condensate I | 4 | 6 | 13.20 | 9.3816616 | 70 |

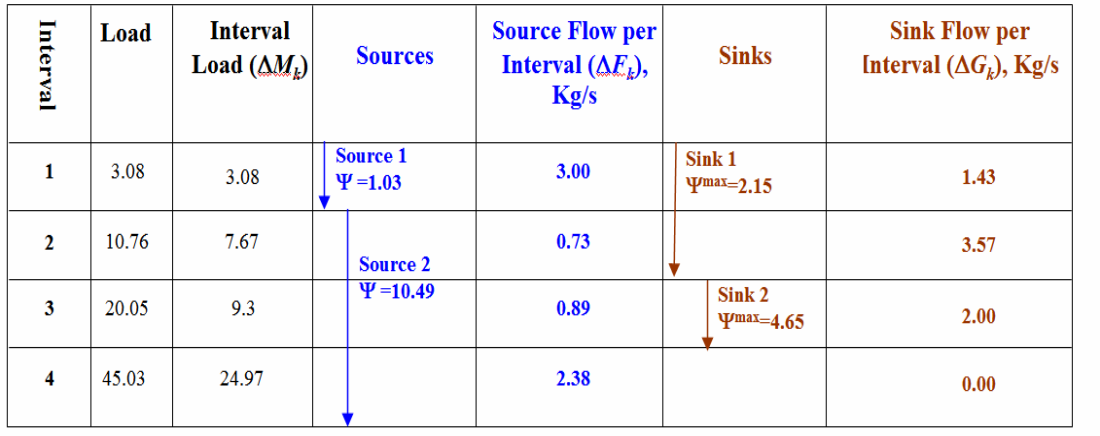


Fig. 35: Property Load Interval Diagram (PLID) for metal degreasing case study.

Next, the cascade diagram with the infeasibilities, along with the revised one, which determines the performance targets directly, can be generated, as shown in Fig. 36. The algebraic method is computationally aligned with the solution found through the property-based pinch technique in the previous chapter. In addition, the property-based pinch location is determined between interval 3 and 4 at the flowrate level of 7Kg/s,

which is consistent with the graphical solution.

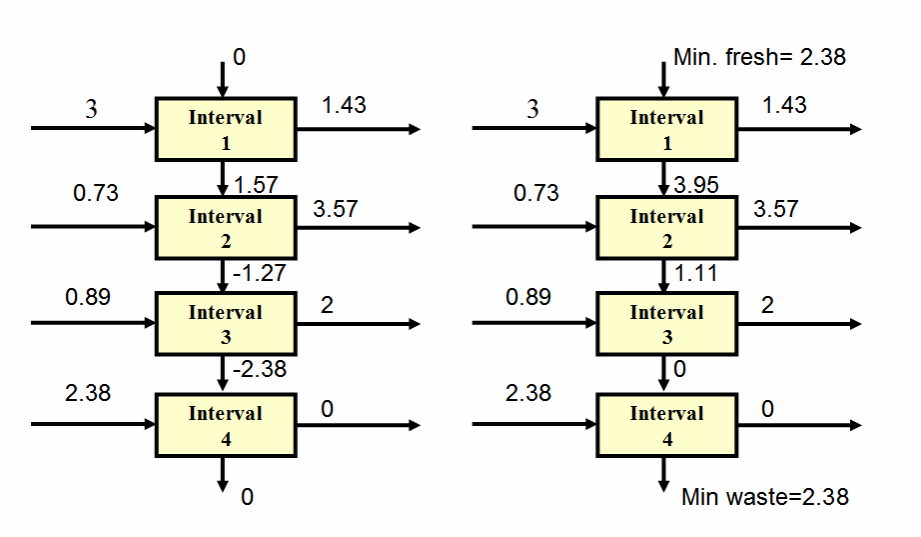


Fig. 36: Property Cascade Diagrams (PCD) for metal degreasing case study.

*Case study II: Waste fiber recycle in papermaking process*

The papermaking process presented in the previous chapter (Fig. 23) is again revisited here (El-Halwagi et al., 2004). It involves two paper machines (paper machines I and II) that demand a certain amount of fiber (bleached pulp), and two available process sources (waste fiber streams - broke) that can be recycled/reused. The key property considered here is again reflectivity. Information on the process sink and source flowrates, property values and constraints are given in Tables 6 and 7. There is also an external fresh source that can be purchased and used to paper machine II in order to supplement the need for fiber feed to the sinks.

It is worth noting here that the fresh fiber feed possesses a reflectivity value of 0.95, which is at the highest level compared to all other limiting operators. In order to minimize the usage of the fresh feed, we shall define the lower bound of the reflectivity value to be the limiting operators of the process sinks. This, in turn, leads to lower limiting loads required by the process sinks (compared to that defined by the upper

bound as the limiting operator). Hence, the upper bound of the operator values in Table 6 is assigned to be the limiting value.

After the required calculations shown in Table 9, the PLID is created as shown in Fig. 37. This is used to generate the cascade diagrams given in Fig. 38. From the revised diagrams it is obvious that the target for minimum use of fresh fiber is 14.95 ton/hr, whereas the target for minimum waste fiber discharge is 24.95 ton/hr In addition, the pinch location is at the zero residual, i.e. between intervals 3and 4 corresponding to a flowrate of 140 ton/hr. These values are in agreement with those found through the visualization procedure in the previous chapter.

Table 9
Data on the papermaking facility case study

| Sink | Flowrate, ton/hr | Reflectivity, R | Operator, Ψ=R^(5.92) | Cum. Mass Flow, ton/hr | Cum. Mass Load, ton/hr |
|---|---|---|---|---|---|
| Paper machine II | 40 | 0.9 | 5.36E-01 | 40 | 2.E+01 |
| Paper machine I | 100 | 0.85 | 3.82E-01 | 140 | 6.E+01 |
| Sources | Flowrate, ton/hr | Reflectivity, R | Operator, Ψ=R^(5.92) | Cum. Mass Flow, ton/hr | Cum. Mass Load, ton/hr |
| Fresh | To be determined | 0.95 | 7.38E-01 | 14.953397 | 1.E+01 |
| Process Fiber | 90 | 0.88 | 4.69E-01 | 104.9534 | 5.E+01 |
| Broke | 60 | 0.75 | 1.82E-01 | 164.9534 | 6.E+01 |

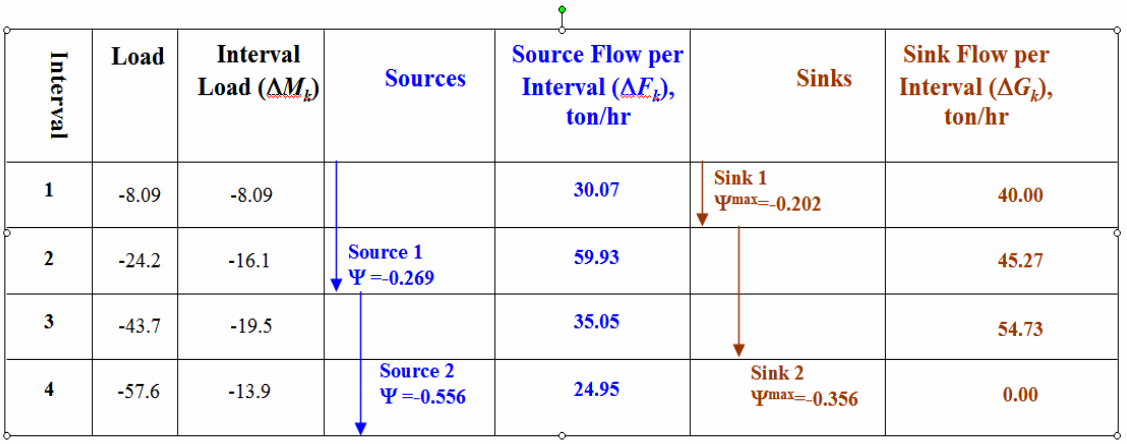


Fig. 37. Property Load Interval Diagram (PLID) for the papermaking case study.

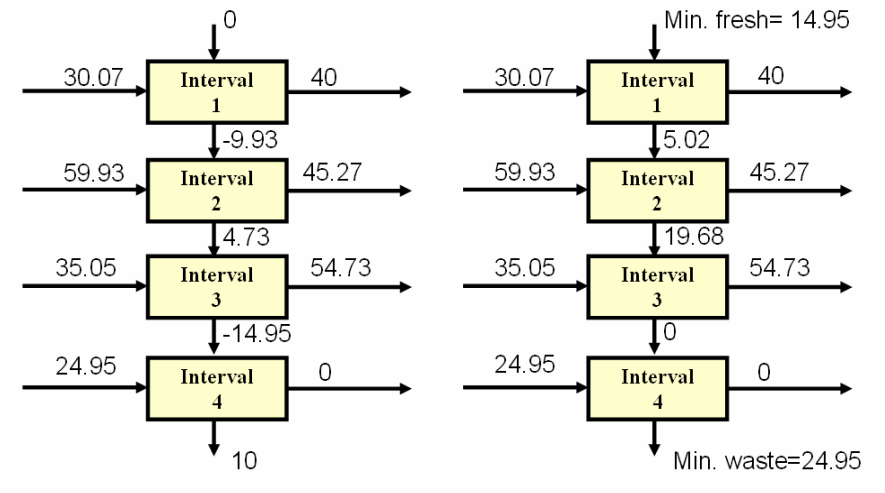


Fig. 38: Property Cascade Diagrams (PCD) for the papermaking case study.

# CHAPTER V
# PROCESS MODIFICATION THROUGH VISUALIZATION TECHNIQUES FOR PROPERTY-BASED INTEGRATION

## 1. INTRODUCTION

While traditional process design is carried out on the basis of individual chemical components, it was previously pointed out that there are many design problems that are component-independent. These problems can be adequately addressed and solved by tracking functionalities or properties that are essential for the process performance within an integrated framework.

There are many examples of design problems that are based on properties or functionalities. For instance, there are constraints on process units that can accept recycled/reused waste and process streams based on the properties of the feeds to processing units. An example of this is a condenser that performs based on vapor pressure.

Moreover, there are common examples of streams, which are continuous mixtures that consist of numerous (almost infinite) chemical species. Tracking each chemical component of these streams is almost prohibitively difficult. Therefore, by designing the process based on properties or functionalities of these streams the numerous chemical constituents do not need to be enumerated.

The novel property-based design paradigm, which has been introduced by Shelley and El-Halwagi (2000), allows the conserved tracking of properties throughout the process by employing the new concept of clustering. Shelley and El-Halwagi (2000) incorporated the clustering technique into a mass integration approach to determine optimal strategies for the recovery and allocation of complex hydrocarbon mixtures.
Moreover, Qin et al. (2004) developed an algebraic procedure for property-based integrated design. Using constraint reduction techniques, they proposed a systematic method for the allocation of process and external sources to sinks based on property constraints that can involve more than three properties.

The current approach uses the clustering concept to identify optimum strategies not only for resource allocation, but also for unit manipulation. In particular, stream properties here are allowed to change according to changes in process variables. However, rigorous bounds for the property search domain need to be determined and optimum allocation and unit manipulation rules are to be derived.

## 2. PROBLEM STATEMENT

The problem to be addressed here can formally be stated as follows:

Given is a process with a certain number of sources (process and waste streams), Ns, which possess a finite number of properties, Np. Each property value of a stream $i$, $p_{p,i}$, is a function of a set of design variables, $\mathbf{d}_{p,i}$ and a set of operating variables, $\mathbf{r}_{p,i}$ that characterize the whole process. The design variables belong to an interval $[\mathbf{d}^{l}_{p,i}, \mathbf{d}^{u}_{p,i}]$ dictated by design restrictions throughout the process. Similarly, the operating variables belong to another interval $[\mathbf{r}^{l}_{p,i}, \mathbf{r}^{u}_{p,i}]$ imposed by operating constraints throughout the system, e.g.

$$\mathbf{d}^{l}_{p,i} < \mathbf{d}_{p,i} < \mathbf{d}^{u}_{p,i} \tag{5.1}$$

$$\mathbf{r}^{l}_{p,i} < \mathbf{r}_{p,i} < \mathbf{r}^{u}_{p,i} \tag{5.2}$$

where $p$ = 1, 2, …, Np and $i$= 1, 2, …, Ns.

Given is also a fresh source, whose cost per unit mass is $C_f$, and a number of process units, Nu, along with their property and flowrate constraints:

$$p^{l}_{p,j} < p_{p,j} < p^{u}_{p,j} \tag{5.3}$$

$$G^{l}_{j} < G_{j} < G^{u}_{j} \tag{5.4}$$

where j = 1, 2, …, Nu.

Our objective is to identify optimal process modification strategies in order to optimize the allocation of the process resources and minimize the fresh consumption, while satisfying all property and flowrate constraints for the process units. In particular, our goals are to develop visualization tools that systematically minimize the fresh consumption for the process and at the same time optimize the design and operating variables that affect the property values of the process sources. Additionally, new fresh

resource substitutes can be investigated by optimizing the process variables and properties of the streams.

## 3. PROPERTY-BASED TECHNIQUES

The proposed property-based approach was first introduced by Shelley and El-Halwagi (2000) and it is based on tracking properties or functionalities of streams by transforming them into conserved quantities known as clusters.

*The clustering concept*

Clusters are surrogate properties that are tailored to possess two main features: intra- and inter- stream conservation. They can mathematically be described as follows:

$$C_{p,i} = \Omega_{p,i} / \mathrm{A}UP_i \tag{5.5}$$

where $\Omega_{p,i}$ is the dimensionless operator derived by dividing the actual operator $\psi_p(p_{p,i})$ by a reference value $\psi_p^{ref}$. The actual operator is a mathematical expression of the property, such as the property's mixing rule can be given by an expression of the following type:

$$\psi_p(\overline{p}_p) = \sum_{i=1}^{Ns} \chi_i \cdot \psi_p(p_{p,i}) \tag{5.6}$$

where $\chi_i$ is the fractional contribution of the $i^{\text{th}}$ stream into the total flow rate of the mixture and $\overline{p}$ is the property value of the mixture. Also, the $AUP_i$ in equation 5.5 denotes the augmented property index for a stream *i* given by the summation of all the dimensionless operators in stream *i*, i.e.

$$AUP_i = \sum_{p=1}^{Np} \Omega_{p,i} \tag{5.7}$$

One can now verify the two conservation rules for the clusters, i.e.:

$$\sum_{p=1}^{Np} C_{p,i} = 1 \qquad \text{(intra-stream conservation)} \tag{5.8}$$

and

$$\overline{C}_p = \sum_{i=1}^{Ns} \beta_i * C_{p,i} \qquad \text{(inter-stream conservation)} \qquad (5.9)$$

where $\overline{C}_p$ is the mean cluster resulting from mixing streams and $\beta_i$ is the cluster lever arm given by the following expression:

$$\beta_i = x_i * AUP_i \,/\, \overline{AUP} \qquad (5.10)$$

The aforementioned conservation characteristics enable the tracking of properties when mapped into the cluster domain.

*Interval analysis*

Interval analysis can be used to develop reliable inclusions for the minimum and maximum values of many functions (Ratschek, and Rokne, 1988).

Some main principles of interval analysis, which are used in this chapter, are described below.

Let I be the set of real impact intervals [a, b], a,b∈ R. Operations in I are defined by the following expression:

$$A*B = \{\alpha*\beta: \alpha\in A, \beta\in B\} \text{ for } A, B\in I \qquad (5.11)$$

where the symbol * stands for any operation (i.e. +, -, ·, /).

The inclusion isotonicity principle from interval arithmetic suggests the following: For A, B ϵ I, if α ϵ A and β ϵ B, then α*β ϵ A*B.

Equivalent to the above definition are the following constructive rules:

$$[a, b] + [c, d] = [a+c, b+d] \qquad (5.12)$$

$$[a, b] - [c, d] = [a-d, b-c] \qquad (5.13)$$

$$[a, b] \cdot [c, d] = [\min(ac, ad, bc, bd), \max(ac, ad, bc, bd)] \qquad (5.14)$$

$$[a, b] / [c, d] = [a, b] \cdot [1/d, 1/c] \text{ if } c,d\neq 0 \qquad (5.15)$$

Interval analysis will be used here to determine the limits of the property values ($p^l_{p,i}$ and $p^u_{p,i}$). Knowing that any stream's property value $p_{p,i}$ is a function of the design and operating variables throughout the process, we have:

$$p_{p,i} = f(\boldsymbol{d}_{p,i}, \boldsymbol{r}_{p,i}) \qquad (5.16)$$

Using inclusion isotonicity of interval arithmetic, we can derive the bounds on the dimensionless operator, $\Omega_{p,i}$:

$$\Omega^{l}_{p,i} < \Omega_{p,i} < \Omega^{u}_{p,i} \tag{5.17}$$

For instance, consider the following empirical expression that gives the density value of a compound as a function of temperature T and pressure P:

$$\rho = \alpha_0 + \alpha_1 T + \alpha_2 P \tag{5.18}$$

where $a_0$, $a_2$ are positive constants, $a_1$ is a negative constant, $T$ takes values from [$T1$, $T2$] and P$\in$ [$P1$, $P2$].

Thus, according to interval rules the upper and lower values that $\rho$ can take are:

$[a_0,\ a_0]+[a_1,\ a_1]\cdot[T1,\ T2]+[a_2,\ a_2]\cdot[P1,\ P2] = [a_0,\ a_0]+[\min(a_1T1,\ a_1T2),\ \max(a_1T1,\ a_1T2)]+[\min(a_2P1,\ a_2P2),\ \max(a_2P1,\ a_2P2)] = [a_0+a_1T2+a_2P1,\ a_0+a_1T1+a_2P2]$ (5.19)

Hence,

$$\rho \in [a_0+a_1T2+a_2P1,\ a_0+a_1T1+a_2P2] \tag{5.20}$$

Consequently,

$$\Omega_{p,i} \in [1/((a_0+a_1T1+a_2P2)*\psi_p^{ref}),\ 1/((a_0+a_1T2+a_2P1)*\psi_p^{ref})] \tag{5.21}$$

Therefore, using the above inclusion isotonicity principle, rigorous bounds on the dimensionless operators $\Omega_{p,i}$ can be derived, since these quantities are functions of the design and operating variables throughout the process.

*Visualization tools*

Visualization tools can now be used as have previously been described by Shelley and El-Halwagi (2000). Interval analysis principles (inclusion isotonicity) can be employed to define rigorous bounds on the attainable zone for the source, while allowing all design and operating variables to change according to process restrictions. Therefore, revised visualization rules will apply to the source's attainable zone and the sink's feasibility region, so as to identify optimum resource allocation, minimum fresh consumption and waste discharge, while optimizing the operating conditions for all process units.

In addition, material substitution strategies can be considered by graphically identifying superior material properties, so that available resources can be optimally allocated to yield mixtures with desirable properties, while minimizing the cost of the fresh at the same time.

Consequently, optimal material properties can be translated into material components, which possess the optimal properties (Eden et al, 2002).

## 4. CASE STUDY: PROCESS MODIFICATION IN A METAL DEGREASING FACILITY

The process flowsheet of the metal degreasing case study described in chapter I is adopted here. In this paragraph, it is desirable to recycle/reuse the process source leaving the degreaser and minimize the fresh usage, while allowing the temperature and pressure of the unit to change according to process constraints. The key properties for characterizing the suitability of a solvent as an acceptable feed for the degreaser are vapor pressure (VP), density (ρ) and sulfur content (S). In particular, vapor pressure and density are functions of temperature and/or pressure. Antoine's equation describes the relationship between the source vapor pressure, VP and temperature, T:

$$\ln(1000VP) = 12.5826 - 2553.3463/(T-4.0498) \quad (5.22)$$

The following empirical equation relates temperature, T and pressure, P of the source with density, ρ:

$$\rho = 976.9038 - 0.9937T + 1.416P \quad (5.23)$$

In addition, the following equation was derived using existing data and regression analysis for sulfur content, S:

$$S = 359.8/T + 0.819P \quad (5.24)$$

In equations (7), (8) and (9) T is in K and P is in MPa.

Tables 10, 11 and 12 indicate the property values for the fresh, the property constraints for the sink and the property boundaries for the source, along with its temperature and pressure constraints respectively.

Moreover, the following mixing rules apply to determine the property values for any mixture:

$$\overline{VP}^{1.44} = x_{fr} \cdot VP_{fr}^{1.44} + x_s \cdot VP_s^{1.44} \quad (5.25)$$

$$1/\ \overline{\rho} = x_{fr} / \rho_{fr} + x_s / \rho_s \quad (5.26)$$

$$\overline{S} = x_{fr} \cdot S_{fr} + x_s \cdot S_s \quad (5.27)$$

Table 10
Fresh properties

| Vapor Pressure, VP (MPa) | Density, ρ (Kg/m$^3$) | Sulfur content, S (wt%) |
|---|---|---|
| 0.0680 | 621.00 | 0.50 |

Table 11
Sink constraints on properties

| Vapor Pressure, VP (MPa) | | Density, ρ (Kg/m$^3$) | | Sulfur content, S (wt%) | |
|---|---|---|---|---|---|
| Min | Max | Min | Max | Min | Max |
| 0.0670 | 0.1060 | 600.00 | 640.00 | 0.00 | 0.80 |

Table 12
Source constraints on properties and process variable bounds

| Vapor Pressure, VP (MPa) | | Density, ρ (Kg/m$^3$) | | Sulfur content, S (wt%) | |
|---|---|---|---|---|---|
| Min | Max | Min | Max | Min | Max |
| 0.0386 | 0.0655 | 670.78 | 689.66 | 1.25 | 1.65 |
| Temperature, T (K) | | | Pressure, P (MPa) | | |
| Min | Max | | Min | Max | |
| 290 | 308 | | 0.1 | 0.5 | |

Next, the problem can be mapped onto the clusters domain using the aforementioned clustering technique. Here the property constraints for a sink can be transformed into constraints on clusters, which in turn define a region of acceptable feed for the sink. In this case study, we focus on the degreaser, since there are no feasible mixtures of source and fresh that pass through the absorber. As Fig. 39 shows, fresh can be mixed with the source (represented by a single point in this case) at the nominal conditions (T=292K and P=0.4MPa). The optimum mixing point is the one that gives the shortest lever-arm

for the fresh and satisfies the flowrate and property constraints at the same time. This point corresponds to a mixture of 87% wt fresh and 13%wt process source at the aforementioned conditions. In this case, the cost reduction is only 13%.

However, if process modifications are considered, the source's feasibility region is obtained by using the inclusion isotonicity principle of interval analysis. In particular, each of the three properties (vapor pressure, density and sulfur content) can first be transformed into clusters. Thus, bounds on properties, which are functions of the operating variables, are transformed into cluster bounds, which define the feasibility region of the source for any pertinent changes in process variables.

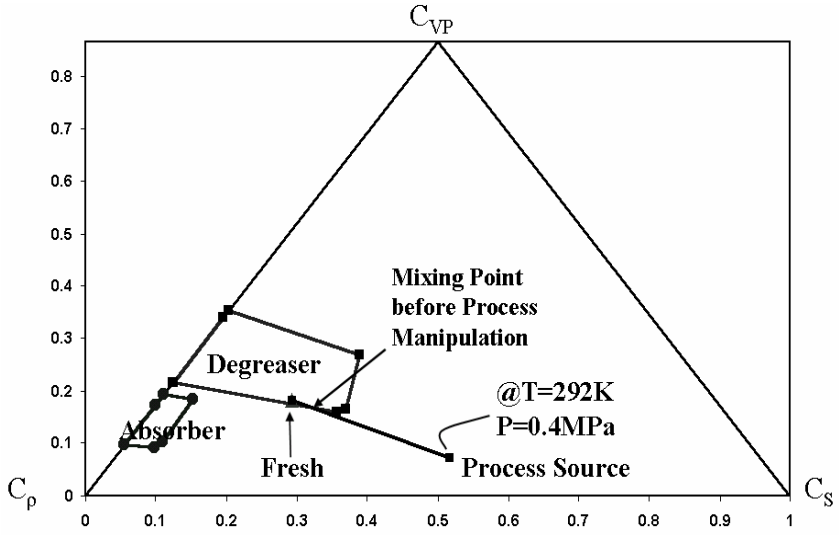


Fig. 39. Ternary diagram for source/sink mapping.

Therefore, fresh can now be mixed with the source at different points within this feasibility region, as can be seen in Fig. 40. There is only one optimum point, though; the point indicated in Fig. 40 that gives the shortest lever-arm among all feasible source points. This point indicates the minimum consumption of fresh, while satisfying the sink's constraints on properties at the same time and corresponds to the following optimal operating conditions: Topt=308K and Popt=0.1MPa. These conditions

characterize the process source with the following properties: VP=0.0655MPa, ρ=670.78 Kg/m$^3$ and S=1.25 %wt.

Thus, the optimal solution suggests the replacement of the degreaser feed with a mixture of 40%wt source and 60%wt fresh, whereas before operating the degreaser at the optimal temperature and pressure, the fresh needed was 87%wt. Therefore, after process manipulation the additional reduction in the cost of fresh is approximately 31%, whereas after considering recycle/reuse and process manipulation the overall reduction in the cost of fresh is 40%.

The flowsheet of the metal degreasing process with the revised configuration for the optimal solution is shown in Fig. 41.

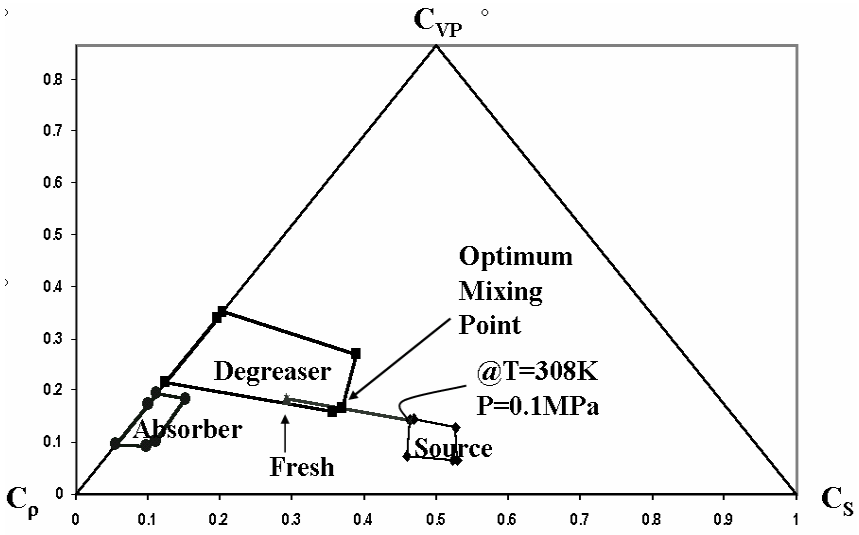


Fig. 40. Ternary diagram for source/sink mapping with process modification.

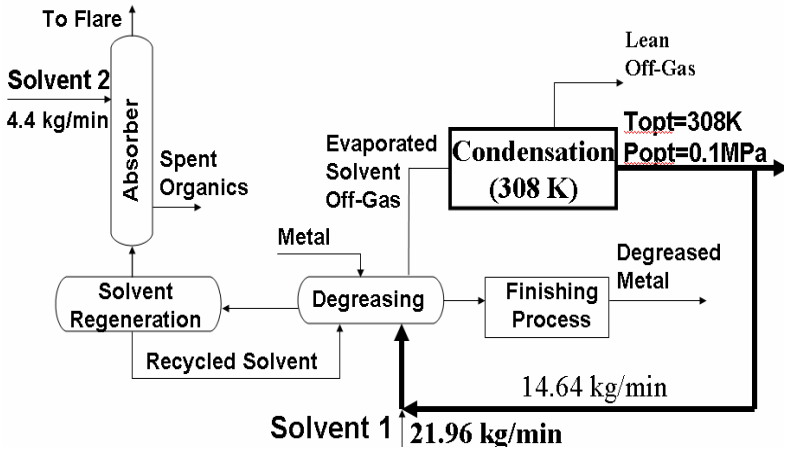


Fig. 41. Process flowsheet at the optimal conditions.

As shown in this chapter, the clustering concept enabled the transferring of the problem from the non-conserved property domain into the component-less cluster domain, whereas interval analysis helped in defining rigorous bounds for properties that are functions of design and operating variables. These bounds are translated into a “trust region of clusters”, which represents the feasible search domain for all possible process modifications. In addition, material substitution strategies may be considered for optimizing both the process and the material performance. Thus, in the next chapter process and material design considerations are examined as an extent to property integration opportunities, which provide a natural framework for integrating process and product design.

# CHAPTER VI
# SIMULTANEOUS PROCESS AND MOLECULAR DESIGN THROUGH PROPERTY CLUSTERING TECHNIQUES – A VISUALIZATION TOOL

## 1. INTRODUCTION

Molecular design and material selection are important activities in optimizing the performance of processing facilities. Numerous contributions have been made in the field of computer-aided molecular design (CAMD). A recent survey of the CAMD field is given by Achenie et al. (2003). In spite of the usefulness of the developed CAMD techniques, they have a common limitation: the targeted properties for the molecules are pre-set based on specific requirements of a certain unit. In so doing, conventional CAMD fails to account for the important input resulting from integrating the process. For instance, the feed to a unit may come from a combination of recycled process streams and external material utilities. The selection of the material utility cannot be made without accounting for the type and extent of recycled process streams. Conversely, the recycle of process streams is dependent on the type of external material utilities to be used in that unit. In addition, the feed to one unit is affected by the performance of preceding and subsequent units.

In assessing the performance of a material utility (e.g., a solvent), one should not only rely on its chemical constituents, but rather on the solvent characteristics and effectiveness for the particular system, namely its properties, such as equilibrium distribution coefficient, critical point, volatility, solubility, density, etc. Since properties form the basis of the performance of many units, they can be primarily considered in order to select solvents, design and optimize a process system. So far, the selection of solvents has been typically carried out through screening of commonly used and already known solvents for particular applications. Previous process design methodologies have been developed by assuming the availability of a certain number of candidate material utilities and without considering material design and substitution options. However, this

could hinder the identification of new molecular structures and/or solvent blends that could achieve a better performance of the system.

Additionally, the selection of solvents aside from the consideration of process integration issues can lead to sub-optimal solutions as a result of ignoring the process interactions. Therefore, solvent selection needs to be considered as a task of selecting a set of properties to target a process performance, and has to be addressed simultaneously through synthesis at the molecular and process level. Process streams may be mixed in an infinite number of ways. Considering all blending possibilities, there are numerous material utilities to be screened before an optimum selection is made. Thus, there is a need in incorporating proper design criteria and constraints, while systematically identifying the optimum set of properties and consequently the optimum molecular structures or mixtures.

This discussion illustrates that in the molecular design problem more consideration needs to be given to process integration opportunities, and CAMD should not be conducted in isolation of process design and vice versa. To date, there is no generic way of simultaneously addressing the design and selection of molecules, as well as the integrated process design. The primary purpose of this work is to fill this critical gap by developing a generic framework and a systematic approach for the simultaneous process and molecular design. Furthermore, particular attention is given to the special case in which a number of molecular groups and molecules with desired features for a specific application are considered, and the resulting candidate molecules that satisfy the process constraints are first visually screened and tested based on their property profiles, and then ranked and chosen according to a CAMP database. For this case, the pertinent working procedures developed emphasize design characteristics and insights that can be obtained by only examining the property cluster diagram, which may also lead to process and molecular synthesis alternatives in optimizing the system.

In addition to the novelty of the framework, the following new contributions are made:

- A consistent property-based interface for the process and molecular design problems
- Formulation and solution of the reverse process-design problem to determine the optimal attainable region for the molecules and the constraints for molecular design
- A systematic technique aiming at identifying new feasible molecules that can be used as external resources and mixed with process resources to optimize the system
- The use of process-integration techniques and group contribution methods to develop valuable insights on process modification and molecular selection
- Demonstration of the special case of "screening and testing" the synthesized molecules based on process and molecular design rules.

## 2. LITERATURE REVIEW

This section provides a selective review of key aspects of two areas: property integration and group contribution methods (GCMs). The task of simultaneously designing integrated processes and molecules can be greatly facilitated by invoking the recently developed area of property integration and componentless design. Recent work done by Shelley and El-Halwagi (2000) has shown that it is possible to tailor conserved quantities, called clusters that act as surrogate properties and enable the conserved tracking of functionalities instead of components. Several papers have addressed the problem of property-based design using graphical tools that guided the synthesis and analysis tasks (Shelley and El-Halwagi, 2000; El-Halwagi *et al.*, 2004; Kazantzi and El-Halwagi, 2004). Moreover, algebraic techniques were developed and employed for property-based integration of systems with more than three properties in concern (Qin *et al.*, 2004). However, these process design methodologies have been developed through commitment to the available process and external resources and without considering material design and substitution options.

Eden et al. (2002, 2004) developed a reverse problem formulation, which allows the determination of molecular-design constraints. However, it was coupled with screening of candidate molecules from a database of known compounds rather than with molecular synthesis. Furthermore, it used rough enumerative mapping to transform the design problem from the property domain to the cluster domain.

Many of the computer-aided molecular design (CAMD) techniques include a step describing structure–property relationships. A commonly-used approach is the group contribution method (GCM) alone or in conjunction with other methods (e.g., Horvath, 1992, Achenie et al., 2003). According to GCM, the property value of a compound is determined by the summation of the individual contributions of the molecular groups forming the molecule. The parameters of the model are determined by fitting the group contribution model to a set of experimental data for a large number of compounds (e.g., Constantinou and Gani, 1994; Gani and Constantinou, 1996). A basic model used in GCM is the one presented by Constantinou and Gani (1994). For the $k^{th}$ property, let $gc_{k,g}$ be the first-order group contribution of the $g^{th}$ functional group which occurs $N_g$ times in a compound $f$. Therefore,

$$\gamma_k(p_{k,f}) = \sum_g N_g * gc_{k,g} \tag{6.1}$$

where $\gamma_k$ is the functional form associated with the GCM property estimation.

To enhance the accuracy of GCMs, Constantinou and Gani (1996), and Marrero and Gani (2001) proposed the usage of more structural information for the molecules as expressed by three levels of group contributions. Several techniques and applications were developed for GCM-based CAMD. These include solvent design (e.g., Odele and S. Macchietto, 1993; Pretel *et al*., 1994, Pistikopoulos and Stefanis, 1998, Giovanoglou et al., 2003; Marcoulaki and Kokossis, 2000), polymer design (Derringer and Markham, 1985; Vaidyanathan and El-Halwagi, 1994; Venkatasubramanian *et al*., 1994), refrigerant design (Sahinidis et al., 2003; Lehmann and Maranas, 2004) and the design of environmentally benign species (Hostrup et al., 1999; Buxton et al., 1999).

## 3. PROBLEM STATEMENT

The problem of material targeting and substitution through property integration, in which only one property is dominant in the process, has been addressed in our previous paper (Qin et al., 2006). Although this case is not rare and sometimes when multiple properties can be lumped as one criterion for process design makes it even more applicable, process design based on multi-property constraints is more often. Because of the restriction of visualization purpose, three dominant properties are chosen to illustrate the methodology, namely, properties *k,* (*k=k1, k2, k3*).

Consider a process with a process sink ($U_J$), which requires a feed with a given flow rate, $G_j$, and an inlet property, $p_j^{in}$, that satisfies the following constraint:

$$p_{k,j}^{l} \le p_{k,j}^{in} \le p_{k,j}^{u} \tag{6.2}$$

where $p_{k,j}^{l}$ *and* $p_{k,j}^{u}$ are the specified lower and upper bounds on admissible values of the $k^{th}$ property entering unit *j*. Furthermore, there is a process mixture of a set of process sources: SOURCES = {ili=1,2,…, $N_{sources}$} that is available to be reused in process sink j. Each source has a known property value, $p_{k,,i}$ , and a flowrate, $F_i$.

Given are also $N_G$ functional groups. Each functional group, g, has a given property contribution $gc_{k,g}$ (*g*=1, 2,…, $N_G$) to the property values of potentially synthesized molecules.

The objectives is to synthesize feasible molecules that can be used to supplement the usage of process sources in the sinks with minimum flowrate of

$$F_{fresh}^{\min} = G_j - \sum_{i=1}^{N_{source}} F_i \tag{6.3}$$

## 4. VISUALIZATION DESIGN APPROACH

*Process-based property clusters*

To solve the simultaneous molecular and process design problem, it is required to invoke the concept of reverse problem formulation to transform process considerations and integration opportunities into property-based constraints for molecular design (Eden

et al., 2002). The reverse property-based material design problem is to identify the feasible properties of all candidate solvents to satisfy the targeted minimum fresh usage. This feasible property region will encompass all the relevant constraints for the molecular design problem. Structural-property relations and group contribution methods will be used to generate a set of feasible molecules that can be used along with the process sources to meet the process constraints. Ternary diagrams based on the cluster concept and basic variable relations in El-Halwagi et al. (2004) will be used here as the bases for the novel mapping approach that interfaces process and molecular design. The core of the visualization method to address the stated problem is to accurately map the feasible property region of candidate solvents and the locus of the candidate molecules.

Before developing our new property-based approach for material design, it is useful to provide a brief overview of the very basic relations regarding the concept of property clusters.

Consider the class of properties whose mixing rules for each raw property are given by the following equation

$$\psi_k(\overline{p_k}) = \sum_{i=1}^{N_s} x_i \psi_k(p_{k,i}) \tag{6.4}$$

where $x_i$ is the fractional contribution of the $i^{th}$ stream into the total flowrate of the mixture and $\psi_k(p_{k,i})$ is an operator on $p_{k,i}$, which can be changed into a dimensionless operator by dividing by a reference value

$$\Omega_{k,i} = \frac{\psi_{k,i}(p_{i,s})}{\psi_k^{ref}} \tag{6.5}$$

Then, an augmented property index (AUP) for each stream $i$ is defined as the summation of the dimensionless raw property operators

$$AUP_i = \sum_{k=1}^{N_c} \Omega_{k,i} \qquad i=1, 2, \ldots, N_s \tag{6.6}$$

The cluster for property $k$ in a stream $i$, $C_{k,i}$, is defined as

$$C_{k,i} = \frac{\Omega_{k,i}}{AUP_s} \tag{6.7}$$

Therefore, one can show intra-stream conservation for clusters:

$$\sum_{k=1}^{N_c} C_{k,i} = 1 \qquad i=1, 2, \ldots, N_s \tag{6.8}$$

Let the cluster lever arm be defined as

$$\beta_i = \frac{x_i AUP_i}{\overline{AUP}} \tag{6.9}$$

where $\overline{AUP} = \sum_{i=1}^{N_s} x_i AUP_i$ (6.10)

Then, one can show inter-stream conservation upon mixing

$$\overline{C}_k = \sum_{i=1}^{N_s} \beta_i C_{k,i} \qquad i=1, 2, \ldots, N_c \tag{6.11}$$

where $\overline{C}_k$ is the mean cluster resulting from adding the individual clusters of $N_s$ streams. Although the mixing of the original properties may be based on nonlinear mixing rules, the clusters are tailored to exhibit linear mixing rules in the cluster domain.

*Delineation of property feasibility regions*

A key point regarding the ternary diagram is the exact mapping of the feasibility region from the property domain to the cluster domain with an exact shape of the feasibility region without enumeration. This problem was already solved in El-Halwagi et al (2004). The boundary of the feasibility region (BFR) can be accurately represented by no more than six linear segments; when extended, the linear segments of the BFR constitute three convex hulls (cones) with their heads lying on the three vertices of the ternary cluster diagram. The six points defining the BFR are determined a priori and are characterized by the following values of dimensionless operators "$\Omega$'s":

$(\Omega_{k1,u}^{\min}, \Omega_{k2,u}^{\min}, \Omega_{k3,u}^{\max})$, $(\Omega_{k1,u}^{\min}, \Omega_{k2,u}^{\max}, \Omega_{k3,u}^{\max})$, $(\Omega_{k1,u}^{\min}, \Omega_{k2,u}^{\max}, \Omega_{k3,u}^{\min})$,

$(\Omega_{k1,u}^{\max}, \Omega_{k2,u}^{\max}, \Omega_{k3,u}^{\min})$, $(\Omega_{k1,u}^{\max}, \Omega_{k2,u}^{\min}, \Omega_{k3,u}^{\min})$ and $(\Omega_{k1,u}^{\max}, \Omega_{k2,u}^{\min}, \Omega_{k3,u}^{\max})$

These features of the BFR are shown in Figure 42.

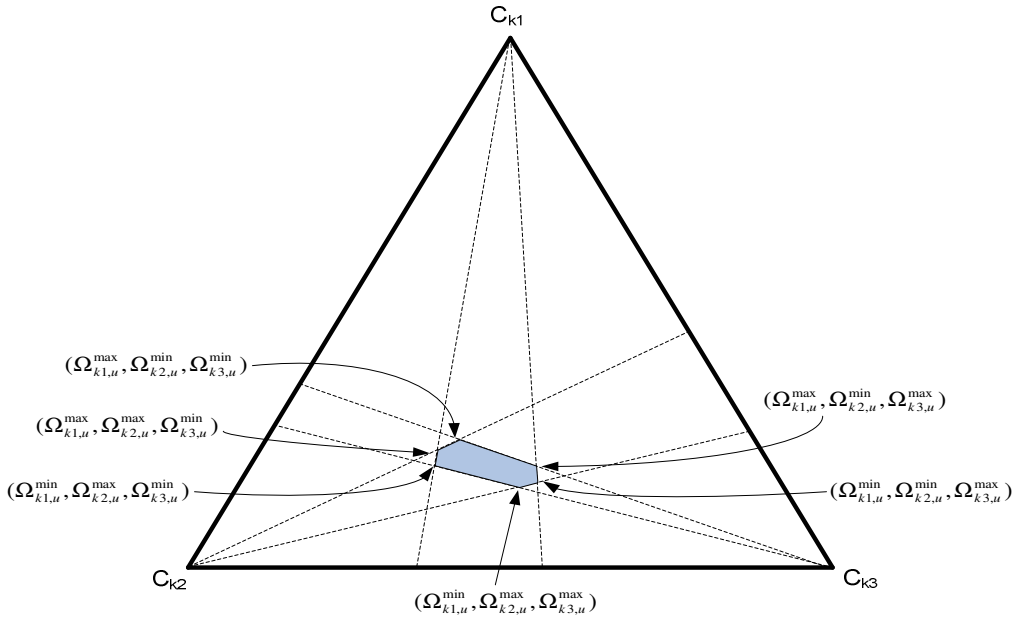


Figure 42. BFR for a process sink on a ternary cluster diagram.

Once the BFR for the original property sink is defined, the property feasibility region for the desired new molecules on the ternary cluster diagram needs to be identified, as well. Let us first define the target for recycle/reuse process sources. Let $x_s^{max}$ be the maximum recycle/reuse fractional contribution over the demand of sinks from the process mixture source with raw properties ($p_{k1,s}$, $p_{k2,s}$, $p_{k3,s}$) which correspond to the dimensionless property operator set ($\Omega_{k1,s}$, $\Omega_{k2,s}$, $\Omega_{k3,s}$). According to the mixing rule, we can get the dimensionless property values $\Omega$ for any points in the property feasibility region as

$$\Omega_{k,f} = (\Omega_{k,u} - x_s^{\max}\Omega_{k,s})/(1 - x_s^{\max}) \tag{6.12}$$

From this expression, we notice that $\Omega_{k,f}^{\max}$ always corresponds to $\Omega_{k,u}^{\max}$, and $\Omega_{k,f}^{\min}$ always corresponds to $\Omega_{i,u}^{\min}$. Thus, according to the BFR method (El-Halwagi et al. 2004), the boundaries of the feasibility region for new molecules is the convex hexagon whose vertices are six points in the following sequence:

$(\Omega_{k1,f}^{\min},\Omega_{k2,f}^{\min},\Omega_{k3,f}^{\max}),(\Omega_{i,f}^{\min},\Omega_{j,f}^{\max},\Omega_{k,f}^{\max}),\quad (\Omega_{k1,f}^{\min},\Omega_{k2,f}^{\max},\Omega_{k3,f}^{\min}),\quad (\Omega_{k1,f}^{\max},\Omega_{k2,f}^{\max},\Omega_{k3,f}^{\min}),$

$(\Omega_{k1,f}^{\max},\Omega_{k2,f}^{\min},\Omega_{k3,f}^{\min})$ and $(\Omega_{k1,f}^{\max},\Omega_{2,f}^{\min},\Omega_{k3,f}^{\max})$. These can be visualized in Fig. 43.

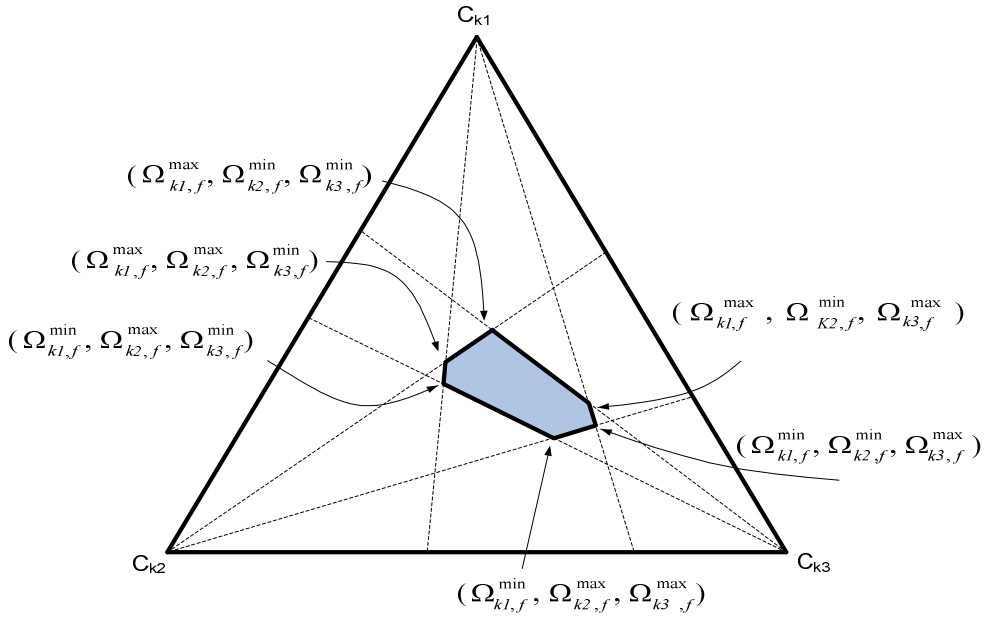


Figure 43. Illustration of the BFR for new molecules.

Equation 6.12 can be geometrically interpreted as follows. The property feasibility region for the new molecules is the projection of the process sink feasibility region with reference at the point of the process source. In detail, if we consider a point on the BFR of the process sink and connect it with the process source, we can obtain a "projection" of this point on the BFR of the new molecules by extending the connecting line to a point that provides a level arm ratio $\beta_s$ which corresponds to $x_s$. Similarly, any point on the process sink BFR can be projected onto a new point on the BFR of the new molecules which provides a level arm ratio of $\beta_s$. This way, the boundaries of the feasibility region for new molecules with a process recycle ratio of $x_s$ can be formed. Previously, it has been demonstrated that the fractional contribution $x_s$ is a

monotonically increasing function of the lever arm ratio $\beta_s$ (El-Halwagi, et al. 2004), i.e. $x_s^{max}$ corresponds to the longest level arm $\beta_s^{\max}$. Thus, we can identify the targeted property feasibility region for new molecules with respect to the maximum recycle, $x_s^{max}$, which is represented by the hexagon with level arm ratio $\beta_s^{\max}$ shown in Fig. 44.

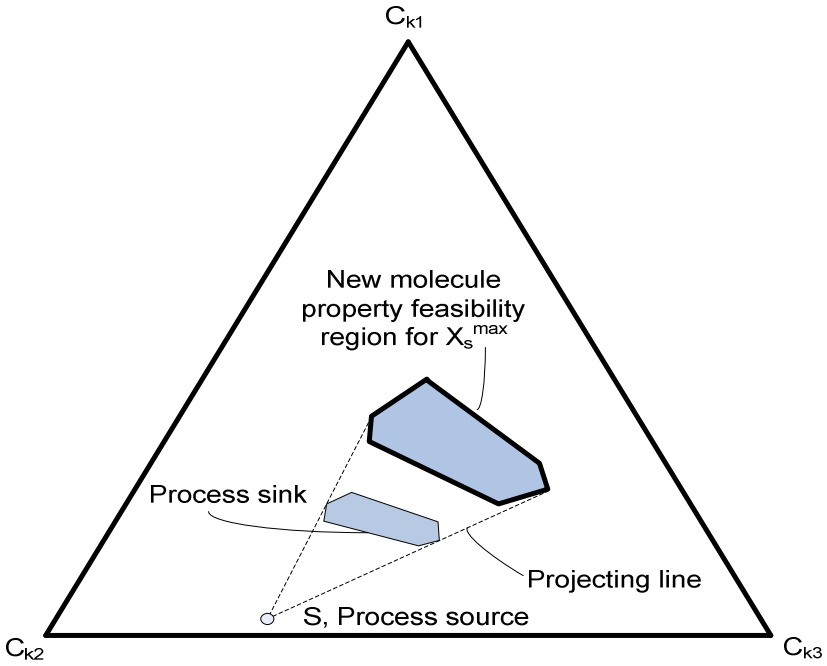


Fig. 44. Delineation of feasibility regions.

After identifying the process-based property feasibility region for new molecules, we move on to define the locus of feasible molecules on a ternary cluster diagram.

*Identification of the molecule locus*

In developing design rules for new synthesized molecules, we need to describe how we can represent them on a ternary cluster diagram. Thus, let us first start with the simple case in which we want to identify the locus of new molecules in a series of

homologous molecules of the following form:

$G_2-(G_1)_{n_1}-G_3$

In this case we know the end groups $G_2$ and $G_3$ of the molecule and we wish to optimize the number $n_1$ of repeating units of the group $G_1$.

It is worth emphasizing here that group $G_1$ may be a branched or composite group of more than one GCM functional groups. In addition, groups $G_2$ and $G_3$ are required functional groups, which along with the intermediate ones provide the required chemistry for the specific process application.

For a new molecule, *m* to be synthesized by three functional groups (g=1, 2, 3), its cluster coordinates need to satisfy the revised "mixing rule" expressed now as follows:

$$C_{k,m}=\sum_{g=1}^{3}\beta_g\cdot C_{k,g} \quad \text{for } k=1, 2, 3 \tag{6.13}$$

where $C_{k,m}$ is the cluster of the synthesized molecule on property *k*, $C_{k,g}$ is the cluster of group *g* on property *k* and $\beta_g$ is the cluster-based lever arm of group *g* given by the following equation:

$$\beta_g = n_g AUP_g / \sum_{g=1}^{3} n_g \cdot AUP_g \tag{6.14}$$

where $n_g$ is the number of occurrences of group g in the molecule *m*.

By using the coordinate correlation derived in El-Halwagi et al. (2004), the cartesian coordinates $X_m, Y_m$ for a molecule synthesized by three molecular groups with individual cartesian coordinates $x_g, y_g$ (*g*=1, 2, 3) satisfy the following expression:

$$Y_m = AX_m + B \tag{6.15}$$

where $A=[AUP_2(y_1-y_2)+AUP_3(y_1-y_3)]/[AUP_2(x_1-x_2)+AUP_3(x_1-x_3)]$ and

$B=[AUP_2(x_1y_2-x_2y_1)+AUP_3(x_1y_3-x_3y_1)]/[AUP_2(x_1-x_2)+AUP_3(x_1-x_3)]$

When four molecular groups participate in the generation of a molecule of the following type:

$G_3-(G_1)_{n_1}-(G_4)_{n2}-G_2$,

then the problem yields more degrees of freedom, and the synthesized molecules must

lie on a line that belongs to a family of lines represented by one parameter (either $n_1$ or $n_2$):

$$Y_m = (n_2 A_1 + A_4) X_m + (n_2 C_1 + C_4)/(n_2 B_1 + B_4) \tag{6.16}$$

where $A_1 = AUP_4(y_1 - y_4)$, $A_4 = AUP_3(y_1 - y_3) + AUP_2(y_1 - y_2)$, $B_1 = AUP_2(x_1 - x_2)$,

$B_4 = AUP_3(x_1 - x_3) + AUP_2(x_1 - x_2)$, $C_1 = AUP_4(x_1 y_4 - x_4 y_1)$,

$C_4 = AUP_3(x_1 y_3 - x_3 y_1) + AUP_2(x_1 y_2 - x_2 y_1)$

These relations can be visualized in Fig. 45.

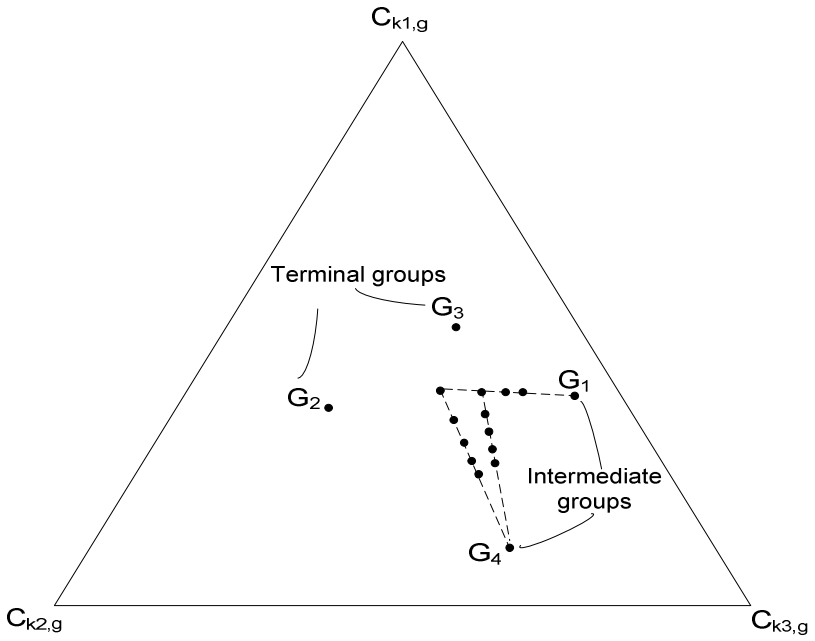


Fig. 45. Identification of the molecule locus.

*Visualization of the correlation between process and molecular design*

After depicting the method to visualize the feasibility region for new molecules from the process viewpoint and the locus of the molecules from the group contribution viewpoint, the correlation between those viewpoints should be explored. Two cases need

to be considered here; one is when the two ternary diagrams can be merged to one through necessary transformations of the property operators, and the other is when it is possible to either map molecules based on their property values onto the process ternary diagram or map the process feasibility region onto the group contribution ternary diagram, if the first case is not applicable.

**Case 1: hybrid graph for process and molecular design with convertible properties**

The key point for this case is that when using one ternary diagram to depict the feasibility region and the molecule locus, it is necessary to make sure that no displacement will happen for both of them with respect to their locations in the two individual ternary diagrams.

The group contribution method for the first level groups provides the following relations for properties such as critical volume ($V_c$), standard Gibbs energy ($G_f$), standard enthalpy of formation ($H_f$), standard enthalpy of vaporization ($H_v$) and standard enthalpy of fusion ($H_{fus}$) (Gani and Constantinou, 1996):

$$p_k - p_{k0} = \sum (N_g * gc_k) \tag{6.17}$$

Equation 6.17 can be converted to the property operator mixing rule expression as follows

$$\overline{\psi}_k = \sum x_g * \psi_{k,g} \tag{6.18}$$

where $\overline{\psi}_k = p_k - p_{k0}$, $x_g = \frac{N_g}{\sum N_g}$, and $\psi_{k,g} = gc_k * \sum N_g$

On the other hand, according to the K-rule (Horvath, 1992), the aforementioned properties also exhibit mixing patterns, which can be expressed mathematically as follows: $p_k = \sum x_i * p_{k,i}$ with little deviation compared to the more complex model. This expression can also be rewritten as:

$$p_k - p_{k0} = \sum x_i * (p_{k,i} - p_{k0}) \tag{6.19}$$

or in property-operator notation:

$$\overline{\psi}_k = \sum x_i * \psi_{k,i} \tag{6.20}$$

Comparing equations (6.18) and (6.20), one can see that property-mixing operators for

both synthesized molecules based on the GCM and stream mixtures in a process system can show the same "mixing" pattern, i.e. $\overline{\psi}_k = p_k - p_{k0} = \sum x_j * \psi_{k,j}$. This characteristic allows us to combine the two ternary diagrams in one, while keeping the distinct connotations of both diagrams. In other words, it is possible to use the hybrid ternary diagram to directly relate the feasibility regions derived from process considerations to the molecular design scheme (molecule locus, molecular group locations, etc.) and vice versa. The hybrid diagram is a useful tool in determining whether there are feasible molecular candidates for the process and how these candidates can be synthesized, and it is shown in Fig. 46.

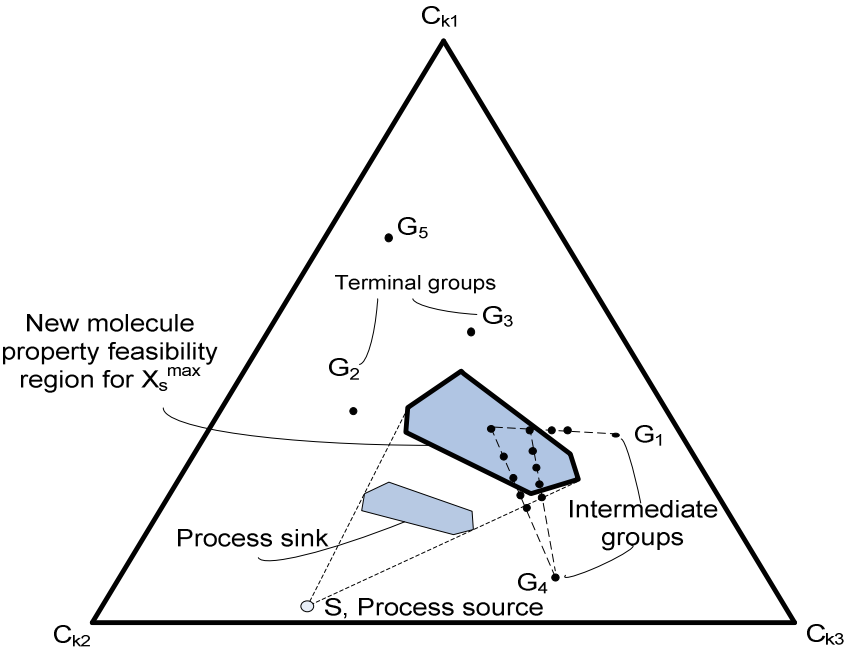


Fig. 46. Hybrid process and molecular design graph.

It is worth mentioning here that the hybrid process and molecular design graph gives the designer a lot of insights;

(1) Certain groups like $G_5$ do not need to be considered as candidate molecules. This is

because in no way they can be combined with the other molecular groups (G2 and G3) to yield a feasible molecule (a molecule that belongs to the feasibility region).

(2) Multiple candidates satisfying the optimal process design may exist; the new candidates are the ones that lie inside the new molecules feasibility region, and the constituent molecular groups, as well as their repeated numbers can be also identified from the graph.

(3) If there is no optimal group candidate or no optimal repeated number, one can search for the next best feasible candidate and so on.

**Case 2: graphical mapping for process and molecular design with inconvertible properties**

This case deals with properties for which the left-hand side of the GCM property-estimation model (i.e. $\gamma_k(p_{k,f})$ in equation 6.1) represents a more complex expression. Typical properties of this case are: the normal melting point $T_m$ whose $\gamma_{Tm}(p_{Tm,f}) = \exp(T_{m,f}/T_{m0})$, the normal boiling point (Tb) with $\gamma_{Tb}(p_{Tb,f}) = \exp(T_{b,f}/T_{b0})$, the critical temperature($T_c$) with $\gamma_{Tc}(p_{Tc,f}) = \exp(T_{c,f}/T_{c0})$, and the critical pressure $P_c$ with $\gamma_{Pc}(p_{Pc,f}) = (P_{c,f}-P_{c1})^{-0.5}-P_{c2}$.

For these properties, it is impossible to convert the left-hand side of the process property-operator mixing rule $\overline{\psi}_k$ into the same expression as in the left-hand side of the GCM property-estimation model of equation 6.1, i.e. $\gamma_k(p_{k,f})$. Thus, in this case an indirect mapping (numerical transformations and then mapping) of either the process feasibility region onto the group contribution ternary diagram or the molecule representations onto the process ternary diagram is needed.

However, it needs to be emphasized here that for even this indirect mapping method, there is again a one-to-one correspondence of the property-cluster points on both the ternary diagrams. This can be proved as follows.

For instance, if we first consider the case of the normal melting point Tm, the first derivative of the $\gamma_k(p_{k,f})$ expression with respect to the property is:

$$\frac{\partial\left[\gamma_{Tm}(p_{Tm,f})\right]}{\partial(p_{Tm,f})}=\frac{\exp(T_m/T_{m0})}{T_m}>0 \tag{6.21}$$

Thus, $\gamma_{Tm}(p_{Tm,f})$ monotonically increases with the increase of Tm, and same conclusions can be made for the normal boiling point, Tb and the critical temperature, Tc.

For the case of the critical pressure, Pc, though, we have:

$$\frac{\partial\left[\gamma_{Pc}(p_{Pc,f})\right]}{\partial(p_{Pc,f})}=-0.5(P_c-P_{c0})^{-1.5}<0 \tag{6.22}$$

Hence $\gamma_{Pc}(p_{Pc,f})$ monotonically decreases with the increase of Pc.

So, in general and for both cases, the conditions for using the BFR method to generate a hexagon representing the feasibility region for molecular design on the group contribution ternary diagram are still valid.

*Matching the AUP to yield feasible molecular structures*

It should be emphasized here that the aforementioned ternary diagrams are cluster ternary diagrams. Therefore, molecules located in the property feasibility region are feasible candidates regarding their property cluster values. However, the feasibility of the synthesized molecules for a specific process is determined by the feasibility of the raw properties or property operators. By inspecting equations 6.5 and 6.7, we can notice that in order to ensure the matching of raw properties or property operators, we need to also ensure that the AUP of the candidate molecule must match the AUP of the actual point of the sink feasibility region at which the molecule is located, in addition to the cluster matching.

Let ($\Omega_{1,fi}$, $\Omega_{2,fi}$, $\Omega_{3,fi}$) be a set of three-property operators of a point $f_i$ ($C_{1,fi}$, $C_{2,fi}$, $C_{3,fi}$) in the sink feasibility region. Based on the definition of the cluster, all property operators of the following form:

$\lambda\Omega_{1,fi}$, $\lambda\Omega_{2,fi}$, $\lambda\Omega_{3,fi}$

correspond to the same sink point, $f_i$. In other word, the point $f_i$ represents all sets of

property operators ($\lambda\Omega_{1,fi}, \lambda\Omega_{2,fi}, \lambda\Omega_{3,fi}$), with $AUP_{fi} = \lambda(\Omega_{1,fi} + \Omega_{2,fi} + \Omega_{3,fi})$, where $\lambda$ is a real-number coefficient.

Property-based constraints for the sink feasibility region dictate that:

$$\begin{aligned} \Omega_{1,f}^{\min} \le \lambda\Omega_{1,fi} \le \Omega_{1,f}^{\max} \\ \Omega_{2,f}^{\min} \le \lambda\Omega_{2,fi} \le \Omega_{2,f}^{\max} \\ \Omega_{3,f}^{\min} \le \lambda\Omega_{3,fi} \le \Omega_{3,f}^{\max} \end{aligned} \tag{6.23}$$

or

$$\begin{aligned} \frac{\Omega_{1,f}^{\min}}{\Omega_{1,fi}} \le \lambda \le \frac{\Omega_{1,f}^{\max}}{\Omega_{1,fi}} \\ \frac{\Omega_{2,f}^{\min}}{\Omega_{2,fi}} \le \lambda \le \frac{\Omega_{2,f}^{\max}}{\Omega_{2,fi}} \\ \frac{\Omega_{3,f}^{\min}}{\Omega_{3,fi}} \le \lambda \le \frac{\Omega_{3,f}^{\max}}{\Omega_{3,fi}} \end{aligned} \tag{6.24}$$

Hence,

$$\lambda^{\min} = Max\left\{\frac{\Omega_{1,f}^{\min}}{\Omega_{1,fi}}, \frac{\Omega_{2,f}^{\min}}{\Omega_{2,fi}}, \frac{\Omega_{3,f}^{\min}}{\Omega_{3,fi}}\right\} \tag{6.25}$$

$$\lambda^{\max} = Min\left\{\frac{\Omega_{1,f}^{\max}}{\Omega_{1,fi}}, \frac{\Omega_{2,f}^{\max}}{\Omega_{2,fi}}, \frac{\Omega_{3,f}^{\max}}{\Omega_{3,fi}}\right\} \tag{6.26}$$

Thus, the upper and lower acceptable values for the AUP of a point $f_i$ in the sink feasibility region are:

$$AUP_{fi}^{\min} = \lambda^{\min}(\Omega_{1,fi} + \Omega_{2,fi} + \Omega_{3,fi}) = Max\left\{\frac{\Omega_{1,f}^{\min}}{C_{1,fi}}, \frac{\Omega_{2,f}^{\min}}{C_{2,fi}}, \frac{\Omega_{3,f}^{\min}}{C_{3,fi}}\right\} \tag{6.27}$$

$$AUP_{fi}^{\max} = \lambda^{\max}(\Omega_{1,fi} + \Omega_{2,fi} + \Omega_{3,fi}) = Min\left\{\frac{\Omega_{1,f}^{\max}}{C_{1,fi}}, \frac{\Omega_{2,f}^{\max}}{C_{2,fi}}, \frac{\Omega_{3,f}^{\max}}{C_{3,fi}}\right\} \tag{6.28}$$

Therefore, as it was emphasized before, any molecule located in the feasibility region with cluster coordinates ($C_{1,fi}$, $C_{2,fi}$, $C_{3,fi}$) is a feasible molecule with respect to the raw property or property operator, if and only if its augmented property operator $AUP_m$

belongs to the range of the AUPs defined by the constraints of the sink feasibility region, i.e. $AUP_m \in \left[AUP_{fi}^{\min}, AUP_{fi}^{\max}\right]$. Moreover, it is worth mentioning that for the molecular design techniques, the molecule positions on the cluster diagram indicate that the solution points are distinct and not continuous as they are for the case of process synthesis, where the stream flowrate and property variables are continuous.

*Special case for screening and testing synthesized molecules*

In this section, emphasis is given in describing a simultaneous process and molecular design technique as a special case of the generic one illustrated before, for selecting the optimum molecule and constituent molecular groups among a set of other feasible candidate molecules for a process system with specific constraints, by screening and testing the resulting molecules.

First let us consider the simple case of representing the sink feasibility region derived by process constraints, along with a number of molecular groups that can be selected by surveying the literature and/or examining their required chemical or physical properties. If all molecular groups selected lie in an area in which no combination of them can offer a feasible molecule or mixture (as shown in Fig. 47a), they can be directly excluded by just visually inspecting them in the hybrid graph. Thus, for the case shown in Fig. 47a, no feasible molecule can be synthesized by the particular GCM groups, because the discrete points that consist the locus of the synthesized molecules lie outside the sink feasibility region, and the molecules can not be directly recycled to the sink.

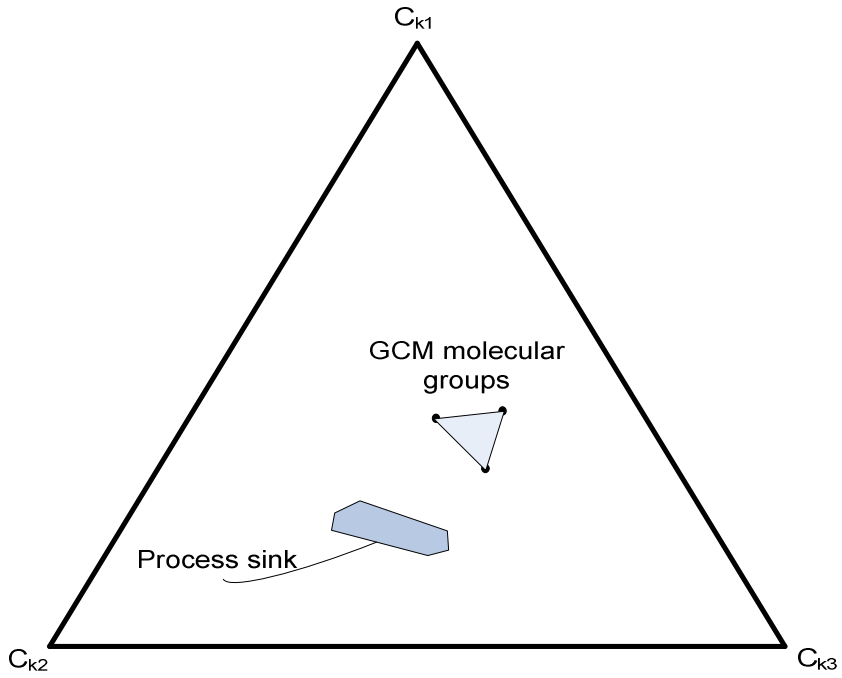


Fig. 47a. Infeasible synthesized molecules.

The same conclusions can be made for the case in which it is desired to recycle a process source or a lumped process source to the sink by mixing it with certain candidate molecules represented in Fig. 47b. Again, no feasible mixture can be found to satisfy the sink's constraints. In other words, the desired properties of any synthesized mixtures can not satisfy the sink's constraints, thus leaving no options for mixing and recycling.

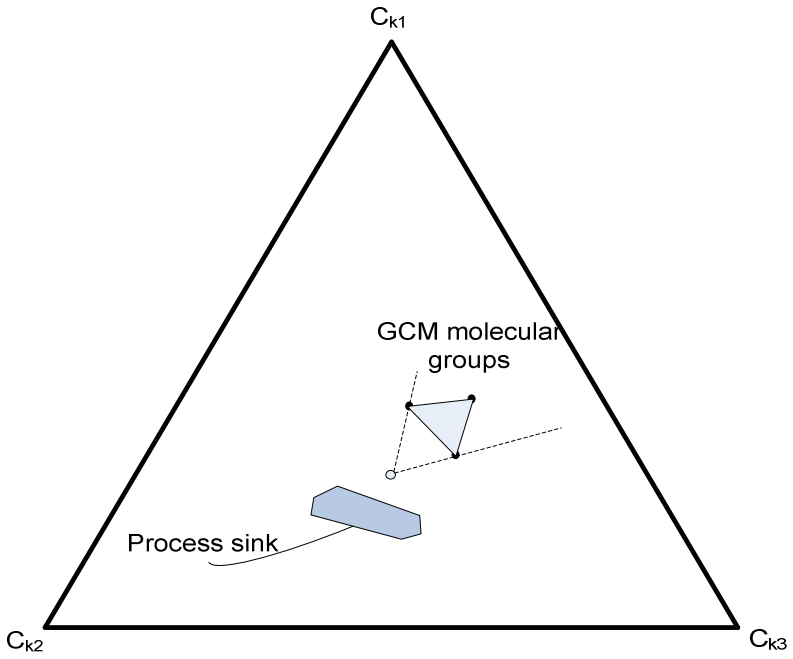


Fig. 47b. Infeasible mixtures.

Thus, a step further featuring an alternative solution of generating and screening molecules by adding functional groups needs to be considered as shown in Fig. 47c. In this graph, we can see that adding more functional groups may yield a new candidate molecule that is more efficient than the ones considered before. In this case, however, it is necessary to look for feasible candidates for which the AUP restriction is also satisfied. This means that even if a new molecule, which yields an optimum mixture to be recycled to the process sink, can be identified, the AUP of this molecule may not match the AUP of the process sink. If that is the case, then the molecule must be excluded, since it does not constitute an actual feasible candidate. Thus, the search of other feasible molecules needs to be directed towards the "next best" molecule that provides the maximum recycle and at the same time satisfies the AUP constraint. On the other hand, if the new molecule satisfies the AUP restriction, then it is considered a feasible candidate molecule, which in turn needs to be evaluated according to other specified criteria.

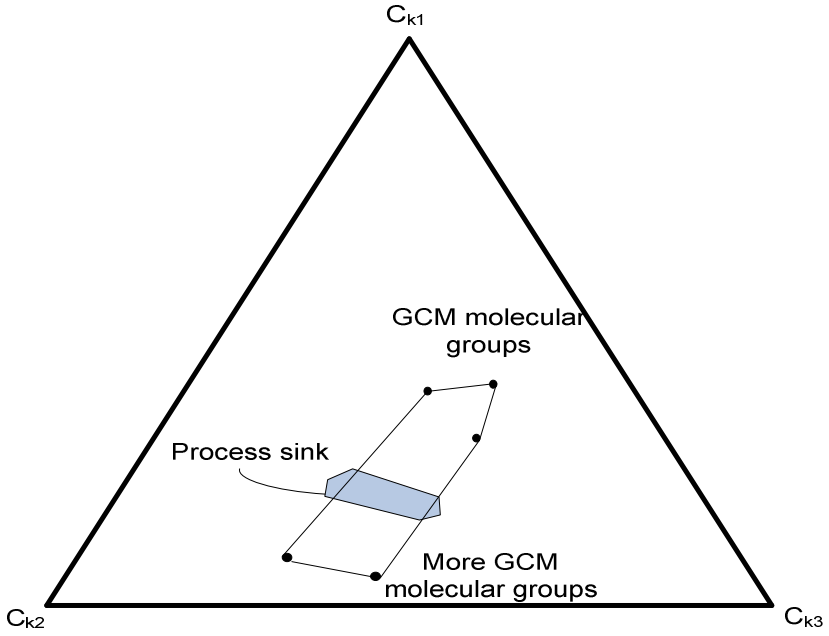


Fig. 47c. Adding functional groups for feasibility.

In addition to the aforementioned methodology, process modifications can be considered to further improve the simultaneous process and molecular design tasks. In particular, changes in the design and/or operating variables can lead to modification of the source properties, which can, in turn, enhance mixing and recycling of process streams and the new molecule candidates. Fig. 47d illustrates how design and operating changes can affect the process source locus to move towards more desirable locations that facilitate mixing and recycling of the process source and the new synthesized molecules.

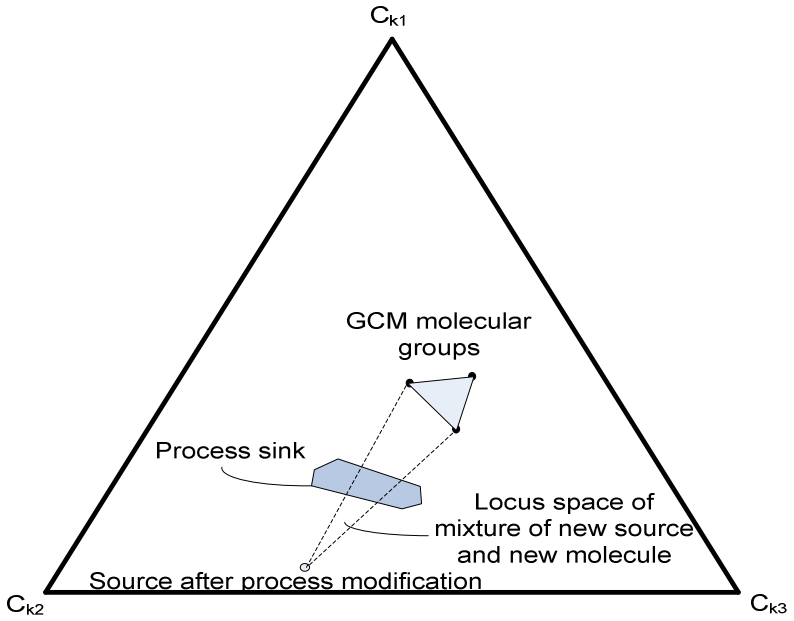


Fig. 47d. Process modification for recycling alternatives.

This procedure offers the advantage of directly visualizing new candidate molecules that can improve the process design and at the same time can be quickly screened, tested and ranked by using the existing databases and CAMD software. Then, the resulting molecules may also be evaluated based on various criteria in an integrated techno-economic analysis, and the optimum one may be chosen.

The aforementioned concepts are illustrated in Fig. 48, in which interrelated steps for an integrated process and molecular design approach are shown.

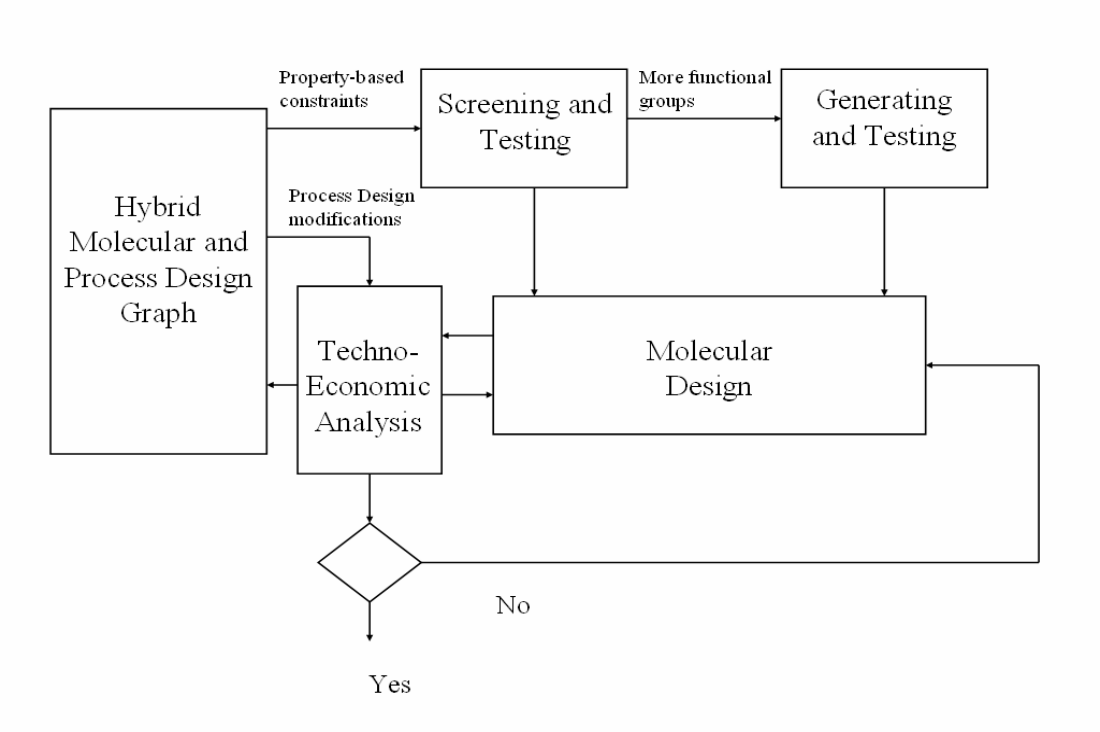


Fig. 48. Integrated process- and molecular- design approach.

## 5. CASE STUDY

Given is an acid gas purification plant with process information listed in Table 13 (group contribution data for the properties considered were taken from Marrero and Gani (2001)). Currently, the process uses two process sources, i.e. S1 and S2 and a fresh resource, which is methyl diethanol amine, MDEA. A new material (homologous to MDEA to implement the chemical reaction) needs to be designed and employed so that process source S3 can be mixed with S1, S2 and recycled back to the system. The properties we consider here are critical volume, enthalpy of vaporization and enthalpy of fusion, which follow linear mixing rules of the following form: $\overline{p}_k = \sum_i x_i * p_{k,i}$.

Table 13
Process data

| Source | Flowrate kmol/h | $V_c$ $cm^3$/mol | $H_v$ kJ/mol | $H_{fus}$ kJ/mol |
|---|---|---|---|---|
| $S_1$ | 50 | 754 | 113 | 15 |
| $S_2$ | 70 | 730 | 125 | 15 |
| $S_3$ | 30 | 790 | 70 | 20 |
| Sink | 300 | [529, 610] | [100, 115] | [20, 24] |
| OH | - | 30.61 | 24.214 | 4.786 |
| $CH_2$ | - | 56.28 | 4.91 | 2.639 |
| $CH_3N$ | - | 94.94 | 9.493 | 6.008 |
| $p_{i0}$ | - | 7.59 | 11.733 | -2.806 |
| | $\overline{p}_k = \sum_i x_i * p_{k,i}$ | | $\overline{p}_k - p_{k0} = \sum_g N_g * p_{k,g}$ | |

According to the given conditions in this case study, the process cluster ternary diagram and the group contribution cluster diagram can be merged to one cluster ternary diagram to show the interaction between process and molecular design. Then, by examining the cluster ternary diagram, all feasible molecules need to be identified. The detailed cluster- and Cartesian- coordinate values of the sink, optimal region, lumped source, GCM functional groups and synthesized new molecules are listed in Table 14.

Table 14
Cluster- and Cartesian- coordinates for graphical representations

| | $C_{Vc}$ | $C_{HV}$ | $C_{Hfus}$ | X | Y |
|---|---|---|---|---|---|
| Sink | 0.3677 | 0.3642 | 0.2681 | 0.4520 | 0.3185 |
| | 0.3512 | 0.3478 | 0.3010 | 0.4766 | 0.3042 |
| | 0.3699 | 0.3131 | 0.3170 | 0.5019 | 0.3204 |
| | 0.4042 | 0.2961 | 0.2997 | 0.5018 | 0.3500 |
| | 0.4231 | 0.3100 | 0.2670 | 0.4785 | 0.3664 |
| | 0.4019 | 0.3445 | 0.2536 | 0.4546 | 0.3481 |
| | 0.3677 | 0.3642 | 0.2681 | 0.4520 | 0.3185 |
| New molecule feasibility region | 0.2331 | 0.4201 | 0.3467 | 0.4633 | 0.2019 |
| | 0.2113 | 0.3807 | 0.4080 | 0.5136 | 0.1830 |
| | 0.2362 | 0.3077 | 0.4561 | 0.5742 | 0.2046 |
| | 0.3225 | 0.2729 | 0.4046 | 0.5658 | 0.2793 |
| | 0.3556 | 0.3009 | 0.3435 | 0.5213 | 0.3079 |
| | 0.3188 | 0.3732 | 0.3080 | 0.4674 | 0.2761 |
| | 0.2331 | 0.4201 | 0.3467 | 0.4633 | 0.2019 |
| Lumped source | 0.4798 | 0.3176 | 0.2026 | 0.4425 | 0.4156 |
| OH | 0.1323 | 0.5231 | 0.3446 | 0.4108 | 0.1145 |
| $CH_2$ | 0.4509 | 0.1967 | 0.3524 | 0.5779 | 0.3905 |
| $CH_3N$ | 0.3914 | 0.1957 | 0.4129 | 0.6086 | 0.3390 |
| MDEA | 0.3165 | 0.3219 | 0.3616 | 0.5198 | 0.2741 |
| MDEA+$CH_2$ | 0.3291 | 0.3102 | 0.3607 | 0.5253 | 0.2850 |
| MDEA+2$CH_2$ | 0.3396 | 0.3004 | 0.3600 | 0.5298 | 0.2941 |
| MDEA+3$CH_2$ | 0.3484 | 0.2922 | 0.3594 | 0.5336 | 0.3017 |
| MDEA+4$CH_2$ | 0.3559 | 0.2852 | 0.3589 | 0.5368 | 0.3082 |
| MDEA+5$CH_2$ | 0.3624 | 0.2792 | 0.3585 | 0.5396 | 0.3138 |
| MDEA+1$CH_3N$ | 0.3291 | 0.3008 | 0.3702 | 0.5347 | 0.2850 |
| MDEA+2$CH_3N$ | 0.3380 | 0.2857 | 0.3763 | 0.5453 | 0.2927 |
| MDEA+3$CH_3N$ | 0.3447 | 0.2744 | 0.3809 | 0.5533 | 0.2985 |
| MDEA+$CH_2$+$CH_3N$ | 0.3387 | 0.2925 | 0.3688 | 0.5381 | 0.2934 |

The graphical solution shows that the resulting candidate molecules, which may satisfy process and molecular constraints are the following: MDEA+0-2($CH_2$) (new molecules formed by adding 0 to 2 -$CH_2$ groups in the MDEA structure), MDEA+$CH_3N$, and MDEA+$CH_3N$+$CH_2$ (Fig. 49).

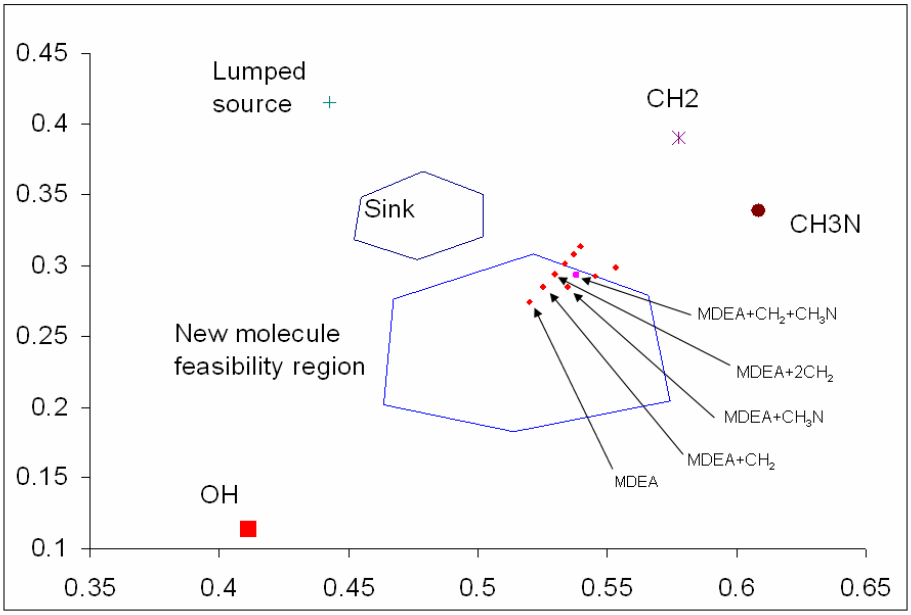


Fig. 49. Graphical identification of candidate molecules.

Next, matching of the AUPs for the candidate molecules need to be examined and verified. Table 15 lists the AUPs of the molecules and the AUP ranges determined by the property constraints of the sink.

Table 15
AUP values for the molecules and ranges based on process requirements

| Candidate molecules | $AUP_m$ | AUP range |
|---|---|---|
| MDEA | 2.41 | [2.47, 2.92] |
| MDEA+($CH_2$) | 2.66 | [2.52, 2.81] |
| MDEA+2($CH_2$) | 2.91 | [2.61, 2.72] |
| MDEA+$CH_3N$ | 2.89 | [2.60, 2.80] |
| MDEA+$CH_3N$+$CH_2$ | 3.14 | - |

Based on the AUP values in Table 15, one can finally conclude that the only feasible molecule among the candidate ones, which satisfies all process requirements is MDEA+$CH_2$ .

# CHAPTER VII
# CONCLUSIONS, FINAL REMARKS AND FUTURE DIRECTIONS

## 1. CONCLUSIONS AND FINAL REMARKS

The dissertation presented here pertains to research in the area of Process Synthesis, Integration and Optimization. It specifically targets a novel area known as "Property Integration", which is defined as a functionality-based, holistic approach to the allocation and manipulation of streams and processing units that is based on tracking, adjusting and matching functionalities throughout the process. Since properties (or functionalities) form the basis of performance of many units, the design techniques need to be able to track key properties instead of key compounds.

Thus, the driving force for developing and utilizing property-based design techniques has been emerged by considering many material reuse problems that are driven and governed by properties or functionalities of the streams and not by their chemical constituency.

The objective was to identify systematic, non-iterative graphical and algebraic procedures that determine the target for minimum usage of fresh resources, maximum material reuse and minimum discharge to waste ahead of any detailed design. In this context, a new property-based material reuse pinch analysis and a non-iterative property-based algebraic procedure were developed, which turned out to become powerful tools in complementing the use of mathematical programming, offering a wide range of insights from targeting and design to process modification opportunities.

In particular, the property-based visualization technique to the maximization of material reuse in the process, which was introduced in chapter III, constitutes a holistic approach to the identification of global, rigorous targets for minimum purchase of fresh resources, maximum integration of process streams and units, and minimum discharge of waste streams. Additionally, the property-based material reuse pinch analysis enables the engineer in making judicious decisions about where to use process resources and to what

extent they should be used. This approach also provides useful insights on process modification for enhanced reuse.

Moreover, the insights from this graphical tool enabled the derivation of a systematic, non-iterative algebraic approach that is conceptually aligned with the parametric programming principles and builds up the mathematical model and programming formulation. Chapter IV has introduced a systematic algebraic procedure that targets material-recycle networks. On the basis of the visualization tool of material-recycle pinch analysis, analogous algebraic constraints were derived. These constraints, along with the optimality conditions, were used to develop a cascade analysis. The cascade diagram calculations result in the identification of rigorous targets on the minimum usage of fresh source and the minimum discharge of waste. Moreover, in order to use the more tedious procedure of rotating the composite representations for sources and sinks, a shortcut technique for eliminating the load resulting from the fresh impurity concentration was developed. This new technique allows the generation of a simple algebraic procedure aiming at determining performance targets for cases in which fresh resources with various key-property values are used.

In addition to the property-oriented graphical and algebraic targeting techniques described in chapters III and IV respectively, a new systematic and integrated design procedure aiming at identifying optimal process modification strategies, in order to optimize the allocation of process sources and minimize waste discharge, was discussed in chapter V. This graphical approach suggested the use of the property clustering concept to map the problem from the non-conserved property domain into the component-less cluster domain. Interval analysis principles were also employed to define rigorous bounds on the process properties of interest, when all allowable changes in design and operating variables were considered. These bounds are translated into a "trust region of clusters", which represents the feasible search domain for all possible process modifications. The search yields optimum strategies for resource allocation, unit manipulation and waste reduction. Strategies for optimizing both process performance

and fresh properties via material substitution were also considered in this part of the dissertation.

It was also emphasized throughout this work that the property integration framework offers a holistic basis and approach to problems that are closely associated to key-properties. In this context, it can also provide a natural environment for integrating process and product design. Traditionally, process design and molecular synthesis problems have been addressed separately leading to sub-optimal results and a severe limitation of the degrees of freedom for the process design and for the molecule selection. However, the challenge of merging the process- and product- associated scales can be of a great merit considering the enhancement of the design efficiency and the identification of new environmentally-friendly material. In this regard, product design can be facilitated by identifying optimum properties of fresh resources, products and/or intermediates, coupled with optimal design solutions.

Towards this direction, a new property-based framework for Simultaneous Process and Molecular Design (SPMD) was introduced in chapter VI. Process requirements and objectives, as well as molecular group properties were interrelated and integrated to simultaneously target process and material design. The new methodology employs property integration tools, along with group contribution methods (GCM) to map the system from the process- level to the molecule- and molecular group- levels, and vice versa. In particular, a common property-based domain was used to relate the two problems, and a reverse-problem formulation is developed to determine property constraints for the molecular design problem. This led to transforming the process considerations to molecular design alternatives. The newly developed property-based graphical method is capable of rigorously identifying distinct regions for the feasible and optimal property profiles and material substitution options.

As a result, the current procedure defines a general framework for screening, as well as for generating a set of candidate molecules that meet the process objective (maximum process source recycle), and can be next evaluated through various performance criteria. It also provides a starting point for addressing problems in integrated process and

molecular design, in which important interrelated features are simultaneously taken into consideration.

In particular, the developed SPMD methodology has provided the following ***novel contributions***:

- A consistent basis for process and molecular design using property integration
- Simultaneous optimization of the process and the molecular design problems without subjugating one objective to the other
- Reverse mapping of the process design problem to determine the constraints needed to define the molecular design problem. This approach enables the decomposition of the process and molecular problems without infringing upon the optimization of the process or the molecules.
- Visualization insights that relate the process performance to the type and number of contributing functional groups to be included in the synthesized molecules
- A systematic way to reconcile the reuse of process resources versus the identification and purchase of external molecules (fresh resources)

This methodology paves the road for many contributions in the area of process and molecular design. The foundations and insights obtained can be used to develop mathematical programming formulations that are computationally effective, can handle higher-dimensional problems, and address broader classes of the problem.

## 2. FUTURE DIRECTIONS

As an extension of the aforementioned simultaneous process and molecular design approach, the design of materials for specific applications can be of a great interest, especially since this design may need to be undertaken in conjuction with material production in an integrated manner. Property integration techniques can efficiently assist such a design by integrating the synthesis tasks. Thus, the design of molecular structures or materials such as biomaterials with targeted properties, safer and nontoxic solvents and separation agents, products being optimally effective yet nontoxic to humans and the

environment, and products and/or by-products that degrade after use are some of the examples regarding an integrated product design framework.

Formulating and addressing design problems of complex systems in material design are very challenging and widely unaddressed issues. Especially now that the new trend in chemical processing industries is moving towards product-oriented processes, the value of complex materials need to be determined primarily by their performance and microstructure and not by their chemical composition. Thus, appropriate material design and optimization techniques, before any experimental process realization, need to be further developed in order to efficiently predict properties of the material at an initial stage and without imposing any cost of experimentation. The conventional way of tackling this problem was first to predict, develop and validate the structure-properties relationship to model systems (especially complex systems) and design the final product, and then to develop an optimally designed production plant. However, a unified framework for dealing with both problems simultaneously would enhance our capability of including all possible design aspects in evaluating, testing and choosing the optimum material and process within an integrated framework. Moreover, these procedures need to take into account both the product quality and environmental concerns. The incorporation of explicit environmentally-related constraints into the design models would be more efficiently achieved by using functionality-based techniques, tools and methodologies. Furthermore, simultaneously addressing material and process design would allow the systematic search for completely new materials, which is substantially important in the advancement of many areas, such as biomaterials, environmentally benign industrial chemistry, and quality management. Thus, the development of new strategies, tools and techniques that are based in process integration and optimization principles, as well as the help of computer software to target the modeling of complex systems in product and process design, is proposed here as a future research direction.

In particular, research in biomaterials is nowdays of an important interest in facilitating life science applications, and has seen substantial growth during the last decades primarily due to the wide range of applications in which they can serve, the

latest advancements in high-throughput screening tools and the development of efficient computational techniques that assist product design. An important challenge in synthesizing functional biomaterials is to obtain tools and techniques for predicting their properties, while the material undergoes conformational changes upon changes in environmental stimuli, such as temperature, pressure, pH etc. Hence, numerical experiments and optimization provide a cheap alternative to physical experiments at the initial steps of the search. There are certain material limitations in developing these systems. Bioavailability of the material and controllability of the system response to thermodynamic changes are major issues in developing structured material design methodologies that hinder the formulation of certain compounds and ensure material purity, bioavailability and controllability. In addition, the design of these systems cannot solely rely on typical group contribution methodologies for predicting properties, since these materials are more complex (block- and graft- copolymers).

Therefore, there is a need to design and optimize multifunctional delivery systems with respect to their desired performance. Methods based on topological or geometric information can be employed for the forward problem solution (predicting properties based on descriptors of materials), whereas property-based integration techniques for process and product design can guide the reverse problem (predicting materials from the desired process performance) to further validate the derived structural model and even yield novel molecular structures to be used in well-specified application systems. The optimization approach would be a case-dependent problem addressing the simultaneous process and product design with proper functional constraints.

In special cases, where the development of an accurate property model needed for this special product design as an intermediate step is a cumbersome task, this can be overcome by solving the reverse design problem, where the unknown design targets will be functions of the target properties. In this context, both the forward and reverse problems can be addressed simultaneously and interrelated to efficiently yield real structure/property relations, as well as appropriate product models and processing systems. The solution strategies can be evaluated after the determination of the optimum

material to meet given performance objective(s). Furthermore, systematic strategies for manipulating the process variables and examining material structure/properties relations could be the focus of further work in this area.

Another area of interest pertaining to property integration is systems biology, which incorporates experimental, computational and theoretical aspects. However, there is an acute need for analyzing, interpreting and integrating data from these aspects into a best-described model that reflects well-established hypotheses, in order to understand the biological response of a system under a wide range of conditions.

This requires the use of systems engineering principles and in particular more sophisticated computational techniques to analyze complex, multivariate data. The complexity of this field emerges from the fact that when modeling these systems, multiple variables, as well as the interactions between them, need to be investigated simultaneously. In addition, these systems include a plethora of components and it is prohibitly difficult to keep track on all of these components. Thus, the need for a better bioprocess analysis, which can be based on functionalities, to address the inherent complexity of the biological processes is essential. The development of such an adequate bioprocess analysis could also facilitate the use of computer-aided techniques.

In this regard, future research attempts would include the development of property-based mathematical models, which will best describe the responses of biochemical systems at a system-level approach. A systematic procedure could be developed in order to formulate multiple competing hypotheses and then test those mathematically to see if they are consistent with experimental data.

To sum up, it is worth emphasizing that there are various promising research directions in the area of property-based process design and integration, which include process operability, integrated process and molecular synthesis, material substitution, and bio-process design. Similar to how mass and energy integration have provided technology breakthroughs, it is believed that property integration will also offer a paradigm shift leading to process and product innovation, resource conservation and sustainable development.

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