

## Novel Group Contribution Based Approach in Process Flowsheet Synthesis, Design and Modelling

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### Abstract

This paper presents the latest developments of a process-group-contribution method to model, simulate and synthesize a chemical process. The process-group (PG) based representation of a flowsheet together with a process “property” model are presented. The PG-based synthesis method is developed using the same principles as the computer aided molecular design methods and gives the ability to generate and screen process alternatives without the need to use the rigorous process simulation models. The process “property” model calculates the design targets for the generated process alternatives while a reverse modelling method determines the design variables matching the target.

**Keywords:** process synthesis, process design, group contribution method

### 1. Introduction

Modelling and simulation of a chemical process usually involve identifying the structure of the flowsheet representing the process, deriving model equations to represent each operation, and solving the resulting total model equations according to one of various available simulation strategies. The flowsheet synthesis problem determines the type of operations and their sequence needed to achieve the conversion of raw materials to some specified set of products. The flowsheet design problem determines the optimal values for the conditions of operation and other operation/equipment related variables for the synthesized flowsheet. The flowsheet modelling, synthesis and design problems are related since for generation and screening of alternatives, some form of flowsheet models are needed. Also, flowsheet models are needed for verification of the synthesis/design problem solution.

In contrast, a group-contribution (GC) based pure component property estimation of a molecule (Marrero and Gani, 2001) requires knowledge of the molecular structure and the groups needed to uniquely represent it. The needed property is estimated from a set of *a priori* regressed contributions for the groups representing the molecule. Having the groups and their contributions together with a set of rules to combine groups to represent a molecule, provides the possibility to “model” the molecule and/or a mixture of molecules. This also means that the reverse problem of property estimation, i.e., the design or synthesis of molecules having desired properties can be solved by generating chemically feasible molecular structures and testing for their properties. This reverse

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problem is also known as computer aided molecular design (CAMD) (Achenie et al. 2002).

Let us now imagine that each group used to represent a fraction of a molecule could also be used to represent an operation in a process flowsheet. Just as in chemical property estimation, groups may have one or more free attachments, in process flowsheet “property” estimation, PGs may also have similar number of free attachments, for example, connecting streams. In this way, a set of PGs representing different types of operations may be created and the “properties” of a particular process flowsheet may be estimated by first identifying the PGs that will uniquely represent it and then by computing their contributions to the needed “property”. Consequently, chemical process synthesis/design problems can be solved through a CAMD-like approach as shown on the general overview of the method (see Figure 1.). It extends the PG-based method for distillation trains (Anterrosches and Gani 2004a) to include new cyclic azeotropic PGs, reactor PGs and mixer PGs within a generic computer aided flowsheet design (CAFD) approach.

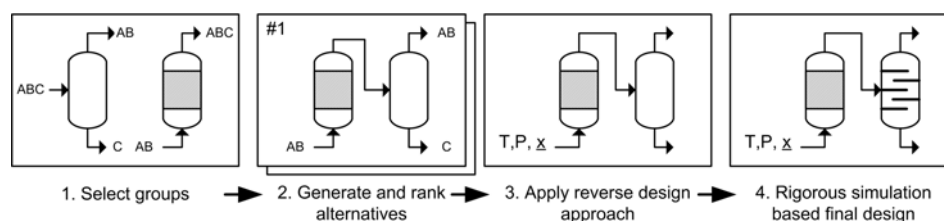


Figure 1. Overview of the framework

## 2. Flowsheet Modelling and Design through Process-groups

To apply a group contribution method for flowsheet synthesis, design and modelling the following has been developed: rules for PG representation of flowsheets, a “property” model for separation process flowsheets and a reverse-model based method for flowsheet synthesis/design.

### 2.1 Definitions (Anterrosches and Gani 2004b)

*Process-group (PG)* - A PG is the representation of one or more unit operations. It has at least one inlet stream and one outlet stream as connections.

*Structure or flowsheet structure* - A structure or a flowsheet structure is defined as the ensemble of process-groups and the connections between the process-groups.

*Flowsheet or process* - A flowsheet or process provides details of the flowsheet structure and the corresponding flowsheet (design/operations) parameters such as stream composition, flowrate, pressure, temperature so that all the needed information for a process are available.

*Flowsheet property* - A flowsheet property is any property that provides a measure of the performance of the operations in the flowsheet and can be expressed as a function of the contributions of one or more unit-operations representing it.

### 2.2 Process-group representation of a flowsheet

Consider a simple process for the reaction of two components A and B to a third component C, which forms an azeotrope with B. The feed mixture is represented by inlet PGs (groups with one attachment), such as (iAB). The end-products (also groups

with one attachment) are outlet PGs, such as (oC) (a pure product or purity  $\geq 98\%$ ). An operation or a set of operations can be represented by a PG having at least one attachment that can be connected to an inlet PG and one attachment that can be connected to an outlet PG, such as (rAB/pABC) – a reactor PG, with A and B as reactants and A, B and C as products or (A/BC) – a separation PG, with A, B and C as inlet and pure A and a BC mixture as outlets. According to the combination rules of PGs (Anterrosches and Gani 2004a) and rules for joining molecular CGs, an outlet of a PG can be connected to the inlet of another PG.

From the list of available PGs like (iAB), (oC), (rAB/pABC), (A/BC), etc., a feasible flowsheet structure can be created as shown in figure 2, where a reaction between A and B takes place forming a third component C, with C and B forming an azeotropic mixture. The products are separated first through a simple distillation column and then by a solvent based separation (represented by a cyclic azeotropic PG). The unused reactants are recycled back to the reactor. As in GC-based molecular property estimation (where the same groups may represent many molecules), the PGs are not component dependent, but component property dependent, thus the ability to use the same group with different components having similar properties.

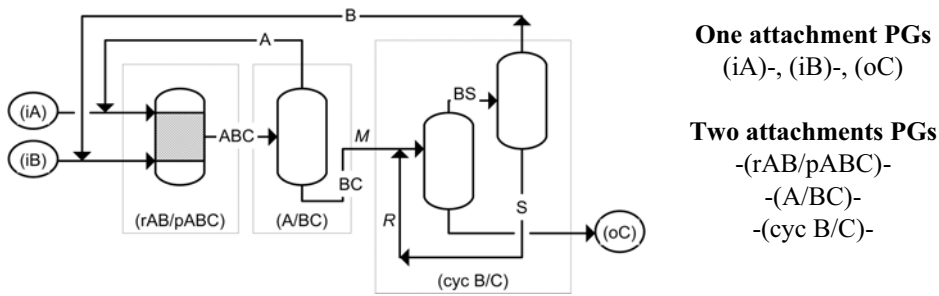


Figure 2. Simple process-group flowsheet representation

### 2.3 Model for driving force approach

The driving force of component  $i$  with respect to component  $j$ ,  $D_{ij}$ , in any operation involving reaction or separation can be modelled through modified driving force expression,

$$D_{ij} = \frac{x_i \beta_{ij}}{1 + x_i (\beta_{ij} - 1)} - x_i = y_i - x_i \quad (1)$$

where  $x_i$  and  $y_i$  are compositions of component  $i$  in two co-existing phases (for separation) or reactant and product (for reaction), respectively.  $\beta_{ij}$  is an adjustable parameter that may be a constant (for example, a constant relative volatility in the case of vapour-liquid separations) or a function of composition (in the case of an azeotropic mixture) or a function of reaction rates (in the case of a reacting system). A set of measured or predicted values of  $\underline{x}$  and  $\underline{y}$  provides the data needed to obtain the driving force model (Eq. 1). As Bek-Pedersen (2004) pointed out, as  $D_{ij} \rightarrow 0$ , no operation is possible while as  $D_{ij} \rightarrow \text{large}$ , operation becomes easy. Also, properties,  $\underline{z}$ , can be identified, which is inversely or directly proportional to  $D_{ij}$ .  $\underline{z}$  is a vector of properties that are needed to maintain  $D_{ij}$ , for example, energy is needed to maintain a VLE system, solvent to break an azeotrope, or catalyst/reagent to promote a reaction.

## 2.4 Reverse approach and flowsheet property model

For operations involving two phases (vapour and liquid) the property needed to maintain  $D_{ij}$  of any separation is heat added to the system. From a design point of view, the goal is to find the point of maximum driving force,  $d_{ij}^k = D_{ij,max} = \overline{D}_i$ , usage. That is, a flowsheet “property” model is needed, to provide a relation between the flowsheet configuration and the maximum driving force usage. This flowsheet “property” has been modelled (Eq. 2) as the energy index  $E_x$  of a flowsheet.

$$E_x = \sum_{k=1}^{n=NG} Q_k = \sum_{k=1}^{n=NG} \left( \frac{1 + p_k}{d_{ij}^k} \times a_k + A \right) \quad (2)$$

where  $E_x$  is the energy index of the flowsheet given in MkJ/hr, for a reference mass flowrate,  $Q_k$  is the total contribution of each PG,  $NG$  is the number of PGs,  $p_k$  the topology factor,  $d_{ij}^k$  the maximum driving force of the  $k^{\text{th}}$  PG,  $a_k$  the contribution of the  $k^{\text{th}}$  PG and  $A$  a constant different for each type of PG.

$$p_k = \sum_{i=1}^{nt} \overline{D}_i \quad (3)$$

where  $nt$  is the number of tasks that should be performed before the task  $k$  in the ideal case and  $\overline{D}_i$  the driving force of task  $i$ . This topology factor,  $p_k$ , is a function of the attainable driving force, which is the  $D_{ij}$  actually used. The reverse approach tries to find designs, if available, that matches (attain) the identified maximum driving force,  $d_{ij}^k$ . The contribution of the PG parameters,  $a_k$ , are normally regressed from experimental data. In the case of a cyclic azeotropic PG,  $a_k$  is a function of the internal recycle flow of the solvent. Every unit operation has a position in the flowsheet where it can “attain” the theoretical maximum driving force  $d_{ij}^k$ . At any other position, the unit operation will attain a lower driving force than the maximum.

## 3. Flowsheet structure evaluation

After the synthesis of feasible flowsheet structures through a CAMD like approach (Anterrosches and Gani 2004a), the property of the structures are easily calculated by application of models described by Eq. 2. The evaluation of the properties of the flowsheet structure is similar to the “test” step in CAMD. The property value is used in a qualitative sense to select the best or the set of best alternatives to a given process synthesis/design problem. At this stage of the design process, it is not necessary to perform mass and/or energy balance calculations with the PG-based method. In step 3 (see Fig. 1), from the PGs and their connections, it is possible to perform simple mass balance and/or energy balance calculations through a shortcut method (Anterrosches and Gani 2004b) in order to establish the set of primary design variables of the generated process flowsheet. This set of design variables represent the minimum number of variables through which a process flowsheet can be completely described (or in other words, all other secondary design variables can be calculated from these). The evaluation of a flowsheet property is performed in virtually no computer time as the

calculations have the same level of complexity as the traditional GC methods for molecular property estimation. Therefore, it is possible to screen a very large number of flowsheet alternatives very rapidly and with few calculations.

## 4. Results

The results presented here highlight the use of an extended set of models and process-groups. In particular, results related to the development and use of cyclic azeotropic PGs are presented.

### 4.1 Cyclic azeotropic PG creation

A new cyclic azeotropic PG has been derived from analysis of azeotropic mixtures to handle solvent based separations. The plots of  $D_{ij}$  as a function of solvent rate (see Fig 3a), the solvent free  $d_{ij}^k$  between Acetone and Chloroform increases as a function of the amount of solvent used. Note that they also depend on the type of the solvent.

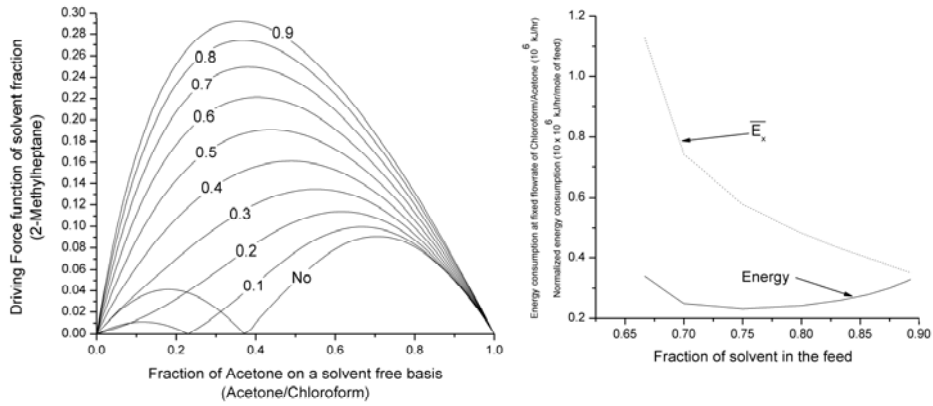


Figure 3. Solvent free driving force (a), energy, normalized energy function of solvent fraction (b)

Considering the flowsheet of a solvent based separation (see (cyc B/C) in Fig. 2), at a given total flowrate  $M+R$ , the energy index of the separation is inversely proportional to  $D_{ij}$ , which as Fig. 3a shows, is related to the amount (recycle  $R$ ) and type of solvent (note that different solvents may match the same  $D_{ij}$  curve). Thus the total contribution of the solvent based cyclic azeotropic PG,  $Q_k$ , can be expressed as:

$$Q_k = \frac{a_k(R)}{d_{ij}^k(R)} \quad (4)$$

Where  $a_k(R)$  is the adjustable parameter  $a_k$  of the property model (Eq. 2) represented now as a function of recycle flow  $R$ , while,  $d_{ij}^k(R)$  is the attainable  $D_{ij}$  represented as a function of  $R$ . As in the development of any GC-based method for molecular property prediction, the parameters  $a_k(R)$  and  $d_{ij}^k(R)$  have been regressed through fitting experimental data. For the purposes of this work, a set of 9 simulations with different recycle flowrate  $R$  has been performed to generate the pseudo experimental data with  $d_{ij}^k(R)$  regressed against the solvent free driving force data (Figure 3a) and  $a_k(R)$  regressed against the normalized energy consumption (Figure 3b)

## 4.2 Design/Simulation results

Consider the separation of Acetone/Chloroform into two pure products, which can be performed with a solvent based separation using a cyclic azeotropic (cyc B/C) PG. A target driving force of 0.33 is selected. Applying CAMD, a list of candidate solvents have been generated, from which, we find that the following two solvents, Benzene and 2-Methylheptane, match this target can be used. The target  $d_{ij}^k$  of 0.33 can be attained with a 2-Methylheptane fraction of 0.7 (we use 2-Methylheptane as it is environmentally more acceptable than benzene) with a reference mass flowrate for the recycle  $R$  of 2.33 kmole/hr. Through Eq. 4, the values of  $Q_k$  and  $R$  needed to match the target  $d_{ij}^k$  is obtained. Note that selection of solvent and  $R$  also fixes  $a_k(R)$ . The energy index  $E_x = 0.138$  is now directly available. At this stage the reverse design approach (step 3, Fig. 1) is performed to obtain the flowrate, temperature, pressure and composition of all the streams using the generated design specifications of the 2 columns in the (cyc B/C) PG. Bek-Pedersen and Gani (2004) provides the needed reverse algorithm. The primary design variables for each column are, reflux, number of stages, feed stage location and top product purity. Using these results as an initial estimate, the final (optimal) design based on rigorous simulation is easily obtained. Figure 3b shows the calculated plots of energy consumption for acetone-chloroform separation as a function of solvent fraction in the feed calculated by rigorous simulation. The results confirm the primary design and that  $\overline{E}_x$  decreases with an increase of  $d_{ij}^k$ . The choice of 0.7 for solvent fraction matches quite closely to the rigorous simulation based optimum solution. The regressed tables of all PGs together with the detailed results from this example and other examples involving reactor PGs can be obtained from the authors.

## 5. Conclusion

The paper has presented a CAMD-like concept of PG contributions for process flowsheet property estimation, synthesis and design. This concept has been transformed into a computer aided tool through the development of a set of PGs representing various types of operations typically found in chemical processes. Properties that may be used as a measure of performance of a process have been identified and modeled as a function of PGs. This has resulted in a CAMD-like approach for CAFD. Current and future work is preparing a set of industrial case studies applying the methodology.

## References

- J. Marrero, R. Gani, 2001, Group contribution based estimation of pure component properties, Fluid Phase Equilibria, 183, 183-208
- L. Achenie, R. Gani, V. Venkatasubramanian, 2002, Computer Aided Molecular Design - Theory & Practice, Elsevier Science B.V., Computer Aided Chemical Engineering 12
- L. d'Anterrosches, R. Gani, 2004, Group Contribution Based Process Flowsheet Synthesis, Design and Modelling, Computer Aided Process Engineering, 18 379-384
- L. d'Anterrosches, R. Gani, 2004, Group contribution based process flowsheet synthesis, design and modelling, Fluid Phase Equilibria, Elsevier, Amsterdam.
- E. Bek-Pedersen, R. Gani, 2004, Design and synthesis of distillation systems using a driving force based approach, Chemical Engineering and Processing, 43, 251-262