Chemical Engineering Science 159 (2017) 106–130

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Designing optimal mixtures using generalized disjunctive programming: Hull relaxations

Suela Jonuzaj, Claire S. Adjiman*

Centre for Process Systems Engineering, Department of Chemical Engineering Imperial College London, London SW7 2AZ, UK

A R T I C L E   I N F O

Keywords:
Mixture design
Generalized Disjunctive Programming
Hull Reformulation
Solubility
Liquid–liquid extraction

A B S T R A C T

A general modeling framework for mixture design problems, which integrates Generalized Disjunctive Programming (GDP) into the Computer-Aided Mixture/blend Design (CAM^{b}D) framework, was recently proposed (S. Jonuzaj, P.T. Akula, P.-M. Kleniati, C.S. Adjiman, 2016. The formulation of optimal mixtures with Generalized Disjunctive Programming: A solvent design case study. AIChE Journal 62, 1616–1633). In this paper we derive Hull Relaxations (HRs) of GDP mixture design problems as an alternative to the big-M (BM) approach presented in this earlier work. We show that in restricted mixture design problems, where the number of components is fixed and their identities and compositions are optimised, BM and HR formulations are identical. For general mixture design problems, where the optimal number of mixture components is also determined, a generic approach is employed to enable the derivation and solution of the HR formulation for problems involving functions that are not defined at zero (e.g., logarithms). The design methodology is applied successfully to two solvent design case studies: the maximization of the solubility of a drug and the separation of acetic acid from water in a liquid–liquid extraction process. Promising solvent mixtures are identified in both case studies. The HR and BM approaches are found to be effective for the formulation and solution of mixture design problems, especially via the general design problem.

1. Introduction

The design of mixtures is an important and challenging problem with numerous industrial applications. Of particular interest are applications in separation processes, such as liquid–liquid extraction (Brignole and Gani, 1983; Karunanithi et al., 2005; Cignitti et al., 2015) and crystallization (Karunanithi et al., 2006, 2009), that require suitable solvents or solvent mixtures to meet given specifications, and where the choice of solvent can have a significant impact on the performance of the process. In drug manufacturing, for example, unsuitable solvents can result in undesired crystal morphology, which may affect downstream processing and product performance (Gordon and Amin, 1984; Karunanithi et al., 2006). Solvent mixtures are also used in chemical reactors to enhance the reaction rate (Folić et al., 2007; Struebing et al., 2013) or (Zhou et al., 2015) and in product design as constituents of the final product formulations (Gani, 2004a, b; Gani and Ng, 2015).

Several systematic methodologies have been developed within the Computer-Aided Mixture/blend Design (CAM^{b}D) framework (Gani, 2004a; Achenie et al., 2003) for the design of solvent mixtures (Brignole and Gani, 1983; Buxton et al., 1999; Sinha et al., 2003; Karunanithi et al., 2005; Cignitti et al., 2015; Jonuzaj et al., 2016), blends of refrigerants (Duvedi and Achenie, 1997; Churi and Achenie, 1997; Vaidyaraman and Maranas, 2002), blends of polymers (Vaidyanathan and El-Halwagi, 1996; Solvason et al., 2009; Zhang et al., 2015), blended liquid products (Yunus et al., 2014) and heat transfer fluid mixtures (Papadopoulos et al., 2013). A more detailed description of the existing methodologies for mixture design can be found in Jonuzaj et al. (2016). In spite of these advances, there remains great potential to improve existing approaches to mixture design within the CAM^{b}D framework. In current practice, the number of compounds or materials required for the design of mixtures or products is often chosen first, before other design decisions are made, and this can lead to suboptimal designs. Thus, most methodologies proposed to date have been focused on the design of mixtures with a pre-specified number of components and have been applied mostly to the design of binary mixtures (Sinha et al., 2003; Karunanithi et al., 2005, 2006; Buxton et al., 1999; Papadopoulos et al., 2013; Vaidyanathan and El-Halwagi, 1996), with some exceptions such as the work of Solvason et al. (2009), Yunus et al. (2014) and Jonuzaj et al. (2016), who have presented methodologies for the design of multicomponent mixtures. CAM^{b}D methods generally rely on Mixed Integer Nonlinear

* Corresponding author.
E-mail address: c.adjiman@imperial.ac.uk (C.S. Adjiman).

http://dx.doi.org/10.1016/j.ces.2016.08.008
Received 30 January 2016; Received in revised form 9 June 2016; Accepted 5 August 2016
Available online 10 August 2016
0009-2509/

Programming (MINLP) techniques to model the discrete decisions inherent in mixture design problems, which are related to the number of components in the mixture and their identities. The solution of the resulting mixed integer optimization problems can be very challenging due to nonconvexities in the space of the continuous variables and a large combinatorial solution space which may lead to several numerical difficulties.

By extending the applicability of CAM^{b}D methods to generalized mixture design problems, in which the number of components in the optimal mixture is not fixed *a priori*, the explicit evaluation of every choice of the number of components can be avoided, making it possible to consider larger design spaces, especially as the number of desirable components increases. This requires developing a comprehensive and systematic mathematical programming approach for the formulation and solution of such problems. In the context of a generalized CAM^{b}D problem, we have recently proposed (Jonuzaj et al., 2016) a novel methodology for determining simultaneously the optimal number of compounds in a mixture, the specific identities of the compounds, and their composition in the mixture. The desired compounds are chosen from a list of possible molecules. Within this approach, logic-based modeling was employed to formulate the CAM^{b}D problem as a Generalized Disjunctive Program (GDP) (Raman and Grossmann, 1994), in order to address the difficulties arising from the complexity of the model and facilitate problem formulation. From this initial work, the objective of our current work is to study different strategies for the solution of the GDP problem, including the Big-M (BM) (Nemhauser and Wolsey, 1999; Raman and Grossmann, 1994) approach and Hull Reformulations (HRs) (Lee and Grossmann, 2000, 2003), in order to circumvent the combinatorial explosion that accompanies large design spaces and facilitate problem solution. The design methodology and the two different relaxation approaches are applied to two case studies of increasing complexity. In the first, simple, example, which involves solid–liquid equilibrium calculations, an optimal solvent mixture that maximizes the solubility of a drug is designed. The second case study consists of a more challenging problem, where the most effective solvent mixture to separate acetic acid from water by liquid–liquid extraction is designed. In both cases, the computational performance of the different reformulation strategies is assessed. As will be seen, the resulting problems are challenging to solve for existing optimization algorithms. Here we focus on the development of a generic formulation, with application to small-scale examples. In practice, the application of the proposed approach to formulation design implies considering a large number of ingredients (e.g., there can be 10–30 ingredients in a typical paint (Nicks and Ryan, 1975) or shampoo (Trüeb, 2007), chosen from a much larger list).

The paper is organized as follows. In Section 2, a brief overview of the GDP concepts necessary for the presentation of the problem formulations and solution strategies is provided. In Section 3, several mathematical formulations of the generalized mixture design problem are presented. Then, in Sections 4 and 5, the proposed approaches are applied to the two case studies.

2. A brief introduction to Generalized Disjunctive Programming (GDP)

In this section we describe briefly the general formulation of GDP problems, which was introduced by Raman and Grossmann (1994), and we review briefly how the GDP problem, with its Boolean variables, can be converted into mixed-integer form so that it can be solved by standard MINLP algorithms (e.g., the outer-approximation algorithm Duran and Grossmann, 1986; Fletcher and Leyffer, 1994). GDP is a logic-based approach for formulating discrete/continuous optimization problems that extends the disjunctive programming proposed by Balas (1985) and involves Boolean and continuous variables that are related via disjunctions, algebraic equations and logic propositions (Beaumont, 1991; Turkay and Grossmann, 1996). It has been employed by Grossmann and co-authors in several applications in the area of process systems engineering, such as the design of process network systems (Raman and Grossmann, 1994; Vecchietti et al., 2003; Ruiz and Grossmann, 2013; Trespalacios and Grossmann, 2015), the design of distillation columns (Grossmann and Trespalacios, 2013), strip-packing (Sawaya and Grossmann, 2005) and scheduling problems (Raman and Grossmann, 1994; Sawaya and Grossmann, 2005; Méndez et al., 2006; Castro and Grossmann, 2012).

The general formulation of a GDP problem involves an objective function to be optimised, general constraints that must hold regardless of the discrete choices, conditional constraints within disjunctions that depend on the discrete decisions, represented by Boolean variables, and logic propositions that connect the disjunctive variables. The general formulation of a GDP problem is presented as (GDP) in Appendix A for completeness. In order to exploit existing MINLP algorithms, once an appropriate GDP formulation has been obtained, it can be converted into an MINLP problem using different approaches, such as big-M or Hull Reformulation, that result in relaxations of varying strength (Lee and Grossmann, 2003; Grossmann and Trespalacios, 2013). The BM formulation (Nemhauser and Wolsey, 1999) is the simplest representation of a GDP problem in a mixed-integer form (Raman and Grossmann, 1994). The concept of a Convex Hull relaxation of a convex GDP problem was introduced by Stubbs and Mehrotra (1999) and was later extended by Lee and Grossmann (2000), Lee and Grossmann (2003), Lee and Grossmann (2005) for the derivation of Hull Relaxations for convex and nonconvex conditional constraints. Generic formulations of the big-M and Hull Relaxation approaches are presented in Appendix A as models (BM) and (HR), respectively. In the (HR) model, disjunctive constraints are transformed into mixed-integer equations via the perspective function, $y_{j,k}h_{j,k}(\nu_{j,k}/y_{j,k}) \leq 0$ (Grossmann and Trespalacios, 2013). In order to avoid the numerical difficulties (division by zero) that can arise from perspective functions, the following approximation was proposed by Sawaya (2006):

$$((1-\epsilon)y_{j,k}+\epsilon)h_{j,k}\left(\frac{\nu_{j,k}}{(1-\epsilon)y_{j,k}+\epsilon}\right)-\epsilon h_{j,k}(0)(1-y_{j,k}) \leq 0 \qquad (1)$$

where $y_{j,k}$ is a binary variable that has one-to-one correspondence with the Boolean variable, $Y_{j,k}$, of model (GDP); $h_{j,k}$ is a nonlinear conditional constraint that depends on the discrete decisions; $\nu_{j,k}$ is a disaggregated variable and ϵ is a small tolerance which usually varies from 10^{-8} to 10^{-2}.

Both (BM) and (HR) have a one-to-one correspondence with model (GDP) (Lee and Grossmann, 2000), so that all three formulations have the same global and local solutions. The BM approach is known to give weak lower bounds in the case of a minimization problem (Grossmann, 2002; Lee and Grossmann, 2003; Vecchietti et al., 2003). This is due in part to the fact that it relies on the Big-M parameter, $M_{j,k}$, a bound whose value cannot always be calculated exactly but is often specified based on an approximate analysis of function ranges. As a result, it is usually given large values, so that feasible points are not excluded from the solution space. The HR formulation, on the other hand, incurs a computational cost due to the introduction of a new set of disaggregated variables, $\nu_{j,k}$, and new constraints, thereby increasing the size of the problem (Lee and Grossmann, 2000). For problems that are convex in the continuous variables, it can be proved (Lee and Grossmann, 2003) that when the discrete domain of the Hull Reformulation is relaxed (i.e. $0 \leq y_{j,k} \leq 1$), it gives bounds that are as tight as or tighter than the bounds generated with the Big-M approach.

Although HR techniques may provide tighter lower bounds than the traditional BM model, they do not always lead to more efficient solution times due to the increased number of variables and constraints (Lee and Grossmann, 2005; Lee and Leyffer, 2012; Grossmann and Trespalacios, 2013). In cases where tight variable bounds are provided, or in large problems where it is desirable not to increase the number of