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Chemical Engineering Science 57 (2002) 2015–2028

Chemical Engineering Science

www.elsevier.com/locate/ces

Linear programming formulations for attainable region analysis

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Received 11 May 2001; accepted 15 January 2002

Abstract

We propose linear programming (LP) models for attainable region (AR) analysis by considering a rate vector field in concentration space with an arbitrarily large number of points. One model provides a method to construct candidate ARs using a fully connected network of continuously stirred tank reactors (CSTRs) of arbitrary volume. More importantly, these methods are extended to derive *linear programming conditions* that are stronger necessary conditions than have proposed previously by Glasser and Hildebrandt. We state the *LP condition* as: *No combination of nonzero volume CSTRs, operating at discretized points in the complement of the candidate AR, can extend the region*. We demonstrate these proposed linear programming techniques on several two-dimensional reaction mechanisms and then apply the LP methods to verify extensions for a previously published three-dimensional candidate AR.

Keywords: Formulations; Linear programming; Mixing

1. Introduction

The attainable region (AR) was originally defined by Horn (1964) as the full set of product composition vectors in $\Re^N$ that can be achieved by all possible steady-state reactor networks, using only the processes of reaction and mixing. In the past 15 years, much work has been devoted to AR research, including that of Glasser, Hildebrandt and coworkers (Glasser, Hildebrandt, & Crowe, 1987; Hildebrandt & Glasser, 1990; Glasser, Hildebrandt, & Crowe, 1990; Glasser, Hildebrandt, & Glasser, 1992; Godorr, Hildebrandt, & Glasser, 1994; Nicol, Hildebrandt, & Glasser, 1997; Glasser & Hildebrandt, 1997). Much of this work focused on geometric interpretations of the fundamental processes such as reaction and mixing for synthesizing reactor networks. Throughout this work, a set of necessary conditions and properties were derived that the AR must satisfy. For reaction and mixing problems, these properties are:

- The AR includes the feed points to the system.
- The AR is convex.
- The process vectors or linear combinations thereof must point into, be tangent, or be zero along the boundary of the AR (except when the AR is constrained, such as with bound on maximum temperature).
- No rate vector in the complement of the AR, when extrapolated back into the AR, can intersect the AR.

The first property is just a definition, as a candidate AR must be constructed from an initial attainable point. The second property follows by including mixing as one of the fundamental processes in the system. The third property follows from geometric interpretations of the process vectors. For instance, if a process vector (e.g. reaction) pointed out of the current AR, that particular process (e.g. reaction in a plug-flow reactor, PFR) could be used to further extend the region. The fourth property excludes the possibility of a single continuously stirred tank reactor (CSTR) from extending the candidate AR.

The AR analysis technique has been applied to many problems including isothermal reactor network synthesis problems (Hildebrandt & Glasser, 1990), nonisothermal reactor network synthesis problems (Glasser et al., 1992; Hopley, Glasser, & Hildebrandt, 1996; Nicol et al.,

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0009-2509/02/$ - see front matter
PII: S0009-2509(02)00101-X

1997), optimal control problems (Godorr, Hildebrandt, Glasser, & McGregor, 1999), reaction and separation problems (Omtveit, Tanskanen, & Lien, 1994; Nisoli, Malone, Michael, & Doherty, 1997) and distillation/separation problems (Kauchali, McGregor, & Hildebrandt, 2000). In contrast, a number of superstructure optimization strategies have been proposed for the direct construction of reactor networks. These include the mathematical programming strategies (Chitra & Govind, 1981; Achenie & Biegler, 1986; Achenie & Biegler, 1990; Kokossis & Floudas, 1990; Kokossis & Floudas, 1991; Smith, 1996; Schweiger & Floudas, 1999; Esposito & Floudas, 1999). However, in these studies, it is not clear whether the superstructure is rich enough to consider all attainable reactor networks. In order to address this question, AR concepts have also been incorporated within mathematical programming models for reactor network synthesis (Balakrishna & Biegler, 1996; Lakshmanan & Biegler, 1996; Rooney & Biegler, 2000; Pahor, Irsic, & Kravanja, 2000). These mathematical programming approaches overcome the geometric difficulties the AR approach encounters in problems with more than three dimensions, making them more applicable to industrial case studies (Lakshmanan, Rooney, & Biegler, 1999; Pahor et al., 2000).

In the above studies, a candidate AR is usually constructed by recursive application of the necessary conditions. Typically, PFRs, CSTRs, and possibly differential sidestream reactor (DSR) trajectories are found from the process feed. Next, the trajectories are convexified using mixing, and places on the boundary are examined where the fundamental processes (or combinations of the fundamental processes) point out of the current region. If such points exist, the region is extended and the search process repeats. If no points are found, the process is terminated. What results is a candidate AR that satisfies the above necessary conditions. What is left unanswered is the question of whether the current candidate AR is indeed the true AR as Horn originally intended it to be. As yet, no general sufficient conditions exist in AR theory.

Some properties of the AR for isothermal reaction and mixing have been formalized by Feinberg and Hildebrandt (1997) and Feinberg (2000a, b). In particular, Feinberg and Hildebrandt (1997) proved that extreme points of the attainable region will always be accessible by means of classical elementary reactor types taken in simple combination. Moreover, the reactors that give rise to these extreme points can be operated in parallel to achieve any realizable reactor product in the attainable region. In his follow-on work, Feinberg (2000a, b) derived additional mathematical conditions that DSRs and CSTRs must obey if they help form the boundary of the AR.

Recent work has focused on automating the AR construction process. Rooney, Hausberger, Biegler, and Glasser (2000) constructed three-dimensional (3D) candidate ARs by finding 2D candidate ARs in orthogonal subspaces and then recombining them sequentially to construct the higher dimensional candidate AR. The key assumption in their work is that CSTRs, PFRs, and mixing lines are sufficient for finding these 2D regions. Although no proof of this assertion exists, the examples solved in the AR literature seem to confirm this assumption. Another systematic method to construct candidate ARs was proposed by Burri, Wilson, and Manousiouthakis (2000). They constructed a 2D region using a linear programming formulation based on CSTRs, PFRs, and mixing lines. This arises from a relaxation of an infinite-dimensional state-space formulation. The problem was decomposed into a distribution network, where all mixing, splitting, recycling and bypassing occurs, and a process operator, where all fundamental unit operations take place.

In the papers of Glasser, Hildebrandt and coworkers, the four necessary conditions listed above are used to check the construction of candidate ARs. Hildebrandt and Glasser (1990) state that such regions *cannot be extended by any combination of PFRs*, *CSTRs*, *recycle reactors and any combination of reaction and mixing*. Unfortunately, this statement is *not true*; the necessary conditions only prevent extensions by reactors considered one at a time. That this statement is incorrect can be seen from Fig. 3, where two "talking CSTRs" extend a candidate attainable region that satisfies the above necessary conditions. The concept of 'talking CSTRs' was first proposed by Feinberg (1991, personal communication to D. Hildebrandt) and Fig. 3 gives an instance of this concept. Here, a PFR trajectory starting from the feed point $(C_a, C_b)=(1,0)$ forms the boundary of a candidate AR that satisfies the necessary conditions above. However, two CSTRs that are fed by the feed point and each other operate at $(0,1)$ and $(1,1)$ and extend this region to the entire concentration space we wish to consider. We will discuss this example in more detail in Section 3.1.

In this work, we derive stronger necessary conditions than the four given above, and these exclude extensions of candidate regions by *combinations of reactors*. We also discuss strategies for constructing such candidate regions. These results are obtained through two new linear programming (LP) formulations for AR analysis. First, a discretization scheme is proposed in concentration space that represents the vector field of rate expressions with an arbitrarily large number of points. A CSTR of any volume is allowed to operate at any of these points and by considering a completely connected network of CSTRs, an LP model for constructing candidate ARs is proposed. In addition, candidate ARs, constructed by any technique proposed in the literature, can now be systematically examined for extensions by a large network of CSTRs, which can also approximate network combinations of other reactor types as well. The rest of this paper is organized as follows. Section 2 presents our LP formulation for constructing candidate ARs. Our necessary conditions are derived from these LPs. This also leads to an efficient and simple test for checking whether candidate ARs satisfy these conditions. In Section 3, we demonstrate the proposed LP formulations on several examples to show the effectiveness of the method. Finally, we conclude the paper in Section 4