Modification of the Conventional Attainable Region and the Formation of a Novel Concept for an Economic Attainable Region

N. Iršič Bedenik and Z. Kravanja

Faculty of Chemistry and Chemical Engineering, University of Maribor
Smetanova 17, Maribor, SI – 2000 Slovenia
Fax: ++ 386 2 25 27 774, e-mail: natasa.irsic@uni-mb.si and kravanja@uni-mb.si

Abstract

The design and optimization of reactor networks using the conventional concept of attainable region is based on technological, rather than, economical criteria. The solution from the economical point of view when the operating and investment costs cannot be neglected may not be optimal, not even in regard to the structure. In order to circumvent this deficiency, the conventional Concentration Attainable Region (CAR) is transformed into an Economic Attainable Region (EAR). A novel concept for EAR construction is proposed first for 2-D, and then for multi-D problems. One-parametric NLP or MINLP optimizations with residence time as a varying parameter are performed to construct trajectories in the EAR. In this way the EAR is aided by mathematical programming for 3-D or more-D problems in order to handle dimensions higher than 2 as degrees of freedom for the economic objective function.

1. Introduction

Efficient design and optimization of reactor networks can be obtained by using the attainable region technique, first introduced by Horn (1964). Trajectories of a plug flow reactor (PFR), a continuous stirred tank reactor (CSTR) and their combinations are basic constitutive elements for an attainable region for 2-D problems (Hildebrandt & Biegler, 1995) and, in addition, a cross flow reactor (CFR) for multi-D problems (Feinberg & Hildebrandt, 1997). This work focuses on a geometric approach for the processes of reaction and mixing in reactor networks. The theory of AR is used for reaction and separation problems (Nisoli, Malone, Michael, & Doherty, 1997) as well as for distillation/separation problems. Some superstructure optimization strategies have been proposed for the construction of reactor networks instead of a geometric approach that involve mathematical programming models for reactor network synthesis (e.g. Aiche & Biegler, 1986). These mathematical programming approaches overcome geometrical difficulties in problems with more than three dimensions.
Since the conventional Concentration Attainable Region (CAR) is constructed using technological criteria (conversion, selectivity, yield, etc.), it does not directly reflect the processes economics. When transforming conventional Concentration Attainable Region (CAR) into an Economic Attainable Region (EAR) that directly reflect the processes economics, it makes them more applicable to industrial case studies (Kravanja et al., 2003). The concept of EAR was first introduced to verify optimal solutions obtained by mixed-integer nonlinear programming (MINLP) and to identify possible profitable extensions to upgrade the superstructure for the next MINLP level (Pahor, at al., 2000). Now, the aim of this work is to expand this concept’s capabilities in order to construct economical attainable regions rather than just to verify solutions, and to upgrade it for multi-dimensional problems using interlinked mathematical programming. This concept is explained by the following steps:

- Basic ideas for transformation of CAR into EAR.
- Procedure for constructing EAR, first for 2-D problems and then some basic ideas for constructing 2-D projections of multi-D problems where dimensions higher than 2 are handled as degrees of freedom by mathematical programming, interlinked to EAR in order to obtain optimal trajectories based on one-parametric NLP or MINLP optimizations and an economic objective function.
- Similarities/differences and advantages/drawbacks using CAR and EAR.
- Incorporation of this novel concept into an MINLP superstructure approach to the synthesis of reactor networks in the overall process schemes.

2. Transformation of CAR Into EAR

Once the Concentration Attainable Region (CAR) is created from a complete set of reactors and their combinations, an optimal solution can be obtained directly from the boundary of the attainable region. Since CAR is constructed using technological criteria (conversion, selectivity, yield, etc.), it does not directly reflect the processes economics. Consequently, the obtained solutions may lie far from the true economic trade-off solution when the investment and operating costs of a reactor network cannot be neglected.

2.1 Illustrative example

The design of the EAR construction will be introduced for autocatalytical reaction (Levenspiel, 1999) $A + A \rightarrow P + A$, with reaction rate vector $R(x)$:

$$R(x) = -k \cdot c_A \cdot c_r$$

(1)

$c_{A0} = 0.99 \text{ mol/l}, \quad c_A = 0.1 \text{ mol/l} \quad \text{and} \quad c_A + c_r = 1$, assuming that in $k = k_s \cdot \exp(-E_a / R \cdot T), \quad k_s = 161.70 \text{ l/(mol} \cdot \text{min}), \quad E_a = 20 \text{kJ/mol}$.

2.1.1 Construction of CAR

First, construction of CAR with technological criteria is performed. The formation of
this region is based on a geometrical approach for all principle types of reactors and their combinations. For 2-D problems CAR is defined using the following procedure:

1. Start from the feed point and work towards the end point by drawing a trajectory of the PFR (Fig. 1, PFR).
2. The PFR trajectory is not a convex region and at this point the reactor vector must be checked. The CSTR trajectory that increases the convex region can be found (Fig. 1, CSTR).
3. Then from the point where the reactor vector of the CSTR becomes a tangent, a PFR trajectory is drawn to the end point (Fig. 1, CSTR+PFR).
4. It should be noted that there is still a small non-convex region at the feed point that can be filled up with the bypass (Fig. 1, bypass).

A combination CSTR+PFR provides the highest concentration for a valuable product (see the border of AR for example at \( \tau = 6 \) min). Note that a Recycle Reactor (RR) trajectory with a fixed reflux ratio (e.g. \( R = 3 \)) lies bellow CSTR+PFR trajectory. In general, the RR trajectory lies between CSTR+PFR and PFR or CSTR trajectories depending on value of \( R \).

---

### Figure 1: CAR for illustrative example.

#### 2.1.2 Construction of EAR

In order to obtain an economically optimal solution in AR, the CAR has been transformed into an EAR by constructing trajectories in economical, rather than concentration spaces, using the economical function:

\[
P(R(x)) = \left[ \sum_{\text{products}} \left( F_{p}^{\text{in}} - F_{p}^{\text{out}} \right) \cdot c_{p} - \sum_{\text{reactants}} \left( F_{r}^{\text{in}} - F_{r}^{\text{out}} \right) \cdot c_{r} - \right]
\]

\[
\sum_{\text{reactants}} \left( y_{i} \cdot c_{\text{in},i} + F_{r}^{\text{in}} \cdot c_{\text{out},i} \right)
\]

Construction of EAR with a known objective function (2) is based on the following procedure:

1) Start the CAR by drawing base reactor trajectories from the feed towards the end point, now taking great care not to skip the RR trajectory. The EAR (Fig. 2) shows that the boundary of the region is defined by a trajectory for CSTR at lower residence time and a trajectory for PFR at higher residence time, and in-between trajectory for the recycle reactor. The chance to define RR with a combination of CSTR + PFR as in CAR gives a worse result for EAR because of the fixed cost that are in the case of CSTR+PFR charged twice to the objective function.

2a) The recycle ratio of the recycle reactor must be optimized at each residence time to obtain a better solution for this system and to overcome non-convexity between RR
and PFR trajectory. This corresponds to a one-parametric NLP optimization with residence time as a varying parameter, recycle ratio as optimization variable and the economic function (2) as the objective function. In this step the 2-D problem (profit and residence time) is transformed into a 3-D problem that produces a convex economical attainable region (Fig. 3) where the third dimension, recycle ratio, is handled by the mathematical programming. The optimal solution obtained in this step is 1149.78 k$/yr. In the same way as recycle ratio, all additional dimensions can be treated by mathematical programming producing 2-D projections of profit vs. residence time or some other varying parameter. In further procedure temperature (2b) and pressure (2c) are selected as additional dimensions. Because of the simplicity of illustrative example they are optimized at feed point and an isothermal reactor is used.

Figure 2: EAR for illustrative example \((R = 3)\).

Figure 3: EAR for illustrative example (optimized \(R\)).

b) The next stage for the EAR construction is the optimization of the temperature and reflux ratio. The EAR has the same boundary as the one in Fig. 3 but the optimal profit of 4-D problem is higher, 1173.36 k$/yr.

c) Problem pass over into 5-D problem with the optimization of three variables. With residence time as a varying parameter NLP optimization of temperature, reflux ratio and pressure yielded an optimal profit of 1174.9 k$/yr obtained with the same boundary as the one in Fig. 3.

Because of fixed cost term, the objective function is not convex which is the basic problem of this new concept of Economic Attainable Region (EAR) theory. Both approaches CAR and EAR are similar in that the optimal solution of the reactor network will be on the boundary of the region. CAR is restricted to 2-D and to 3-D problems but with EAR we can overcome this so that several 2-D projections of the multi-D problem are made which are solved using NLP or MINLP optimization. Some of similarities/differences, advantages/drawbacks between CAR and EAR will be introduced by an industrial example using adiabatic, non-isothermal and cross flow reactor (CFR).
3. Incorporation of the EAR Concept Into an MINLP Superstructure Approach

Implementation of the new Economic Attainable Region (EAR) concept presents itself in the industrial problem of allyl chloride manufacturing described in Kravanja et al. (2003). Two consecutive reactions are $A + Cl_2 \xrightarrow{k_1} B + HCl$ (principal one) and $B + Cl_2 \xrightarrow{k_2} C + HCl$ and one parallel reaction $A + Cl_2 \xrightarrow{k_3} D$ (A propene, B allyl chloride, C 1,3 – dichloro propene, D 1,2 – dichloropropane; $k_{1,0} = 1.5 \cdot 10^{-6}$ s$^{-1}$, $k_{2,0} = 4.4 \cdot 10^8$ s$^{-1}$, $k_{3,0} = 100$ l·mol$^{-1}$·s$^{-1}$, and $E_1 = 66271$ J/mol, $E_2 = 99410$ J/mol, $E_3 = 33140$ J/mol). The reaction rate vector $\mathbf{R}(x)$ for components A, B, C, D and Cl$_2$ is:

$$\mathbf{R}(x) = \begin{bmatrix} -k_1 c_A \cdot c_{Cl} - k_2 c_A \cdot c_{Cl} - k_2 c_B \cdot c_{Cl}, \\ -k_2 c_B \cdot c_{Cl}, \\ k_3 c_A \cdot c_{Cl}, \\ -k_3 c_B \cdot c_{Cl} - k_3 c_A \cdot c_{Cl} \end{bmatrix}$$

The objective is to maximize annual profit at a fixed production of allyl chloride (7,560 mol/s). The EAR is defined using one-parametric NLP or MINLP optimizations of different reactor/process structures from process superstructure (Fig. 4), which comprises all principal types of reactors and most of their combinations.

3.1 Construction of the EAR for PFR

One-parametric MINLP optimization of multi-D problem with residence time as a varying parameter and 35 degrees of freedom as optimization variables was carried out. In case of a heat-integrated process structure and adiabatic plug flow reactor an optimal solution yielded profit of 20,349 M$/yr. In case of non-isothermal reactor the one-parametric MINLP optimization yielded a profit of 20,479 M$/yr. In this way 2-D projections were obtained, Fig. 5. Analysis between adiabatic and non-isothermal reactor shows that for the construction of EAR it is better to use a non-isothermal reactor because of the higher optimal solution.
The same single parametric MINLP optimization as for PFR was used for non-isothermal CSTR with optimal solution 19.845 M$/yr. One-parametric MINLP optimization for a recycle reactor with a fixed recycle ratio gives an RR trajectory under the EAR boundary but with a decreasing of the recycle ratio trajectory it is drawn nearer to the PFR trajectory. Trajectory of the DSR is placed above non-isothermal PFR trajectory because one side flow was selected. Figure 6 shows the final EAR for the process of allyl chloride manufacturing with trajectories for non-isothermal reactors. In this way, all the basic reactor trajectories for the construction of EAR are defined. The boundary of the region is defined with the DSR. The optimal solution is 20.5047 M$/yr at residence time 42.9 s.

4. Conclusion

CAR gives a reactor structure with which reaction equilibrium can be achieved while EAR defines structure and conditions for reactor networks that are optimal from economical point of view. A new one-parametric MINLP optimization approach for the construction of EAR reduces the influence of non-convexities on global optimal solutions. Fixed cost terms in the cost functions favors multiple usage of one-process equipment, e.g. recycle reactor (RR) rather than combination of CSTR+PFR.

References