Synthesis of Optimal Chemical Reactor Networks

C. A. Schweiger and C. A. Floudas[1]

Department of Chemical Engineering, Princeton University, Princeton, NJ 08544-5263, USA

Abstract–The synthesis of optimal reactor networks using a superstructure based approach is considered. The fundamental units in the superstructure are the continuous stirred tank reactor (CSTR) and a cross flow reactor (CFR). The mathematical modeling leads to an optimal control formulation which is solved using a control parameterization technique. The approach is applicable to general reaction mechanisms and is applied to a complex nonisothermal reaction problem.

INTRODUCTION

The goal of reactor network synthesis is to determine the types, sizes, and operating conditions of the reactor units as well as the interconnections among them which transform the given raw materials into the desired products. Previous approaches for addressing this problem can be classified as either superstructure based methods or targeting methods. The superstructure based methods employ a fixed reactor network which includes all the possible networks of interest. This approach was first introduced by Jackson (1968) who postulated a network of parallel plug flow reactors (PFRs) interconnected with sidestreams. Further developments were made by Achenie and Biegler (1986, 1990) where nonlinear programming techniques were used to solve the problem. A reactor network superstructure incorporating continuous stirred tank reactors (CSTRs) and PFRs with various interconnections was considered by Kokossis and Floudas (1990, 1991, 1994). The PFRs were approximated by a series of equal-sized sub-CSTRS and integer variables were used to represent the existence of the reactor units. The resulting formulation was a large-scale, complex, nonconvex mixed-integer nonlinear program (MINLP).

One of the limitations of the superstructure approach is that the solution obtained is only as rich as the proposed superstructure. Increasing the richness comes at the cost of increasing the complexity of the model. To address this issue, targeting approaches were developed based on the attainable region concept first introduced by Horn (1964). The attainable region is the set of all possible conditions that can be obtained through reaction and mixing. These methods determine a target on the performance index for the reactor network regardless of the reactor types and configuration. These techniques were explored as geometric problems by Glasser et al. (1987), Hildebrandt et al. (1990), and Hildebrandt and Glasser (1990). Mathematical programming techniques for the targeting approach were explored by Balakrishna and Biegler (1992a,b).

This work focuses on addressing two disadvantages of the superstructure based approaches: the large, complex formulations and the approximation of the PFR by algebraic models. The PFR is modeled using differential equations and differential sidestreams are used to enhance the richness of the superstructure. The mathematical modeling leads to an optimal control problem which is solved using a control parameterization technique.

REACTOR NETWORK SUPERSTRUCTURE

The reactor network superstructure must be sufficiently rich without becoming unnecessarily complicated. Feinberg and Hildebrandt (1997) showed that the only reactor types that are required to achieve all possible compositions for a given reaction are the PFR, CSTR, and differential sidestream reactor. Thus, the reactor network design is a question of how to incorporate traditional reactors and not a speculation of alternative devices. The fundamental reactor units considered are the CSTR and a cross flow reactor (CFR) unit. The CFR shown in Figure 1 is a PFR with differential entering and leaving sidestreams. The reactor network superstructure consists of the CSTR and CFR units along with mixers and splitters and is based on the principles discussed in Floudas (1995) and Schweiger and Floudas (1998).

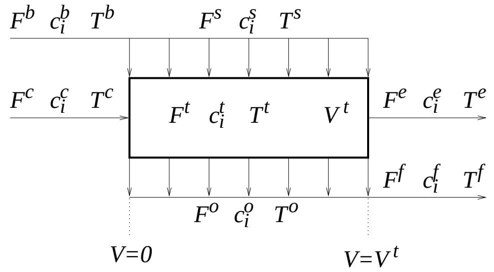

Figure 1. Cross Flow Reactor

[1]Author to whom all correspondence should be addressed.

The mathematical model for the superstructure includes the material and energy balances for all of the units in the superstructure. Algebraic relationships are derived for the CSTRs, mixers, and splitters. However, differential equations are required for the CFR, and the overall formulation is a system of differential and algebraic equations (DAEs).

The superstructure and model are developed for general situations. Although no constant density or ideal gas assumptions need to be made, some closure relationship is required to fully specify the model. The reaction information is supplied in terms of the stoichiometric matrix for the independent set of reactions (ν_{ij}) and the rate of reaction j ($r_j = f_j^r(c_i, T)$). This expression can have forms based on power laws or Langmuir-Hinshelwood kinetics and the temperature dependence is usually described by the Arrhenius law. The rate of production or consumption of species i is given by the product of ν_{ij} and r_j.

For the modeling of the CFR, the assumptions made are steady on-dimensional flow, instantaneous mixing of the sidestreams, and no axial diffusion. The material balance is

$$\frac{d(c_{k,i}^t F_k^t)}{dV} = c_{k,i}^s \frac{d\bar{F}_k^s}{dV} - c_{k,i}^t \frac{d\bar{F}_k^o}{dV} + \sum_{j \in J} \nu_{i,j} r_{k,j}^t \tag{1}$$

where $c_{k,i}^t$ is the molar concentration of species i within reactor k, $c_{k,i}^s$ are the molar concentration in the feed sidestream, and F_k^t is the reactor volumetric flowrate. The differentials $\frac{d\bar{F}_k^s}{dV}$ and $\frac{d\bar{F}_k^s}{dV}$ are the differential flows from the feed sidestream and to the exit sidestream. By permitting differential heating/cooling along the CFR, the energy balance is

$$\frac{d(H_k^t \rho_k^t F_k^t)}{dV} = H_k^s \rho_k^s \frac{d\bar{F}_k^s}{dV} - H_k^t \rho_k^t \frac{d\bar{F}_k^o}{dV} + \frac{dQ_k^t}{dV} \tag{2}$$

where H_k^t and ρ_k^t are the molar enthalpy and molar density within reactor k, and H_k^s and ρ_k^s are the enthalpy and density of the side feed stream. The differential $\frac{dQ_k^t}{dV}$ is the heat flow rate into the reactor.

The initial conditions for these equations are the feed conditions to the CFR:

$$\begin{aligned} c_{k,i}^t\Big|_{V=0} &= c_{k,i}^c \\ F_k^t|_{V=0} &= F_k^c \\ H_k^t|_{V=0} &= H_k^c \end{aligned} \tag{3}$$

The exit conditions of the CFR are matched to the outlet stream through constraints imposed when $V = V^t$:

$$\begin{aligned} c_{k,i}^t\Big|_{V=V^t} &= c_{k,i}^e \\ F_k^t|_{V=V^t} &= F_k^e \\ H_k^t|_{V=V^t} &= H_k^e \end{aligned} \tag{4}$$

To fully specify the model, closure relations are required to determine the enthalpy and density of the various streams in the model. These equations of state are generally functions pressure, temperature, and composition. A detailed presentation of the modeling of the superstructure in provided in Schweiger and Floudas (1998).

OPTIMAL CONTROL SOLUTION FRAMEWORK

By selecting a number of dynamic variables equal to the number of degrees of freedom for the dynamic problem, an optimal control formulation results:

$$\begin{array}{rrcl} \min & J(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{u}(t_i), \boldsymbol{x}) & & \\ \text{s.t.} & \boldsymbol{f}(\dot{\boldsymbol{z}}(t), \boldsymbol{z}(t), \boldsymbol{u}(t), \boldsymbol{x}, t) & = & \boldsymbol{0} \\ & \boldsymbol{c}(\boldsymbol{z}(t_0), \boldsymbol{x}) & = & \boldsymbol{0} \\ & \boldsymbol{h}'(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{u}(t_i), \boldsymbol{x}) & = & \boldsymbol{0} \\ & \boldsymbol{g}'(\dot{\boldsymbol{z}}(t_i), \boldsymbol{z}(t_i), \boldsymbol{u}(t_i), \boldsymbol{x}) & \leq & \boldsymbol{0} \\ & \boldsymbol{h}''(\boldsymbol{x}) & = & \boldsymbol{0} \\ & \boldsymbol{g}''(\boldsymbol{x}) & \leq & \boldsymbol{0} \\ & \boldsymbol{x} & \in & \mathcal{X} \subseteq \mathbb{R}^p \\ & t_i & \in & [t_0, t_N] \end{array} \tag{5}$$

where J is the objective function, $\boldsymbol{f}$ are the DAEs, $\boldsymbol{c}$ are the initial conditions, $\boldsymbol{g}'$ and $\boldsymbol{h}'$ are the point constraints, and $\boldsymbol{g}''$ and $\boldsymbol{h}''$ are the time-invariant constraints. The variables in the problem are dynamic, $\boldsymbol{z}$, time invariant, $\boldsymbol{x}$, and control variables, $\boldsymbol{u}$. The independent variable is t which corresponds to the volumetric position along the reactor (V). The control variables selected are the sidestream flowrates and the CFR temperature which are to be determined as functions of the position along the reactor.

The optimal control problem is solved using a control parameterization approach that converts the problem to a nonlinear program (NLP) where the DAEs are decoupled from the optimization. This approach is described in Vassiliadis et al. (1994). Although the solution of the DAEs con be computationally expensive, by decoupling them from the optimization problem, the algorithm utilizes the features of integration techniques. The integrators automatically adjust the number of steps and their size and are well-suited for handling complex, stiff DAEs.

The control variables, $\boldsymbol{u}$, are expressed as functions of the independent variable, V, and time invariant parameters. A convenient choice for the parameterization function is a Lagrange polynomial. These are interpolating polynomials where the parameters determine the shape of the control variable profile and become optimization variables for the NLP problem. The time horizon is divided into intervals with the controls defined as polynomials over each interval. This allows for piecewise constant expressions, piecewise linear, piecewise quadratic, etc.

By applying the control parameterization, the control variables are eliminated from the problem at the expense of additional DAEs for the control parameterization equations and additional time invariant variables, $\boldsymbol{x}$, for the control parameters. The resulting problem is an NLP in the space of the time invariant variables, $\boldsymbol{x}$ where the objective and point constraints are implicit functions through the integration of the DAE system. The function evaluations and gradients with respect to $\boldsymbol{x}$ are required for J,

$\boldsymbol{h}'$, $\boldsymbol{g}'$, $\boldsymbol{h}''$, and $\boldsymbol{g}''$. For $\boldsymbol{h}''$, and $\boldsymbol{g}''$, analytical expressions can be obtained. However, for J, $\boldsymbol{h}'$, $\boldsymbol{g}'$ the function evaluations and gradients are determined as implicit functions of $\boldsymbol{x}$ through the solution of the DAE system. Integrating the DAE system along with the variational equations provides the values of the state variables at the time instances, $\boldsymbol{z}(t_i)$, as well as the gradients $\frac{d\boldsymbol{z}}{d\boldsymbol{x}}$. With this information known, the functions J, $\boldsymbol{g}'$, and $\boldsymbol{h}'$ are evaluated directly, and the gradients are determined by applying the chain rule:

$$
\begin{aligned}
\frac{dJ}{d\boldsymbol{x}} &= \left(\frac{\partial J}{\partial \boldsymbol{z}}\right)\left(\frac{\partial \boldsymbol{z}}{\partial \boldsymbol{x}}\right) + \left(\frac{\partial J}{\partial \boldsymbol{x}}\right) \\
\frac{d\boldsymbol{h}'}{d\boldsymbol{x}} &= \left(\frac{\partial \boldsymbol{h}'}{\partial \boldsymbol{z}}\right)\left(\frac{\partial \boldsymbol{z}}{\partial \boldsymbol{x}}\right) + \left(\frac{\partial \boldsymbol{h}'}{\partial \boldsymbol{x}}\right) \qquad (6) \\
\frac{d\boldsymbol{g}'}{d\boldsymbol{x}} &= \left(\frac{\partial \boldsymbol{g}'}{\partial \boldsymbol{z}}\right)\left(\frac{\partial \boldsymbol{z}}{\partial \boldsymbol{x}}\right) + \left(\frac{\partial \boldsymbol{g}'}{\partial \boldsymbol{x}}\right)
\end{aligned}
$$

In the reactor network synthesis problem the reactor volume needs to be optimized. This volume is determined by the limits on the integration which are fixed in the control parameterization approach. To allow the volume to vary, the independent variable is scaled and the integration is performed over this scaled variable. The scaling factor becomes a variable which can be optimized. For example, consider the differential equation

$$\frac{dz}{dt} = f(z, x)$$

The variable t can be scaled using the relation

$$t = \tau \bar{t}$$

where $\bar{t}$ is the scaled time and τ is the scaling factor. Substituting this into the differential equation results in

$$\frac{dz}{d\bar{t}} = \tau f(z, x)$$

where τ is now a variable for the optimization. By choosing the limits of the scaled time in an interval to be 0 and 1, the scaling parameter becomes the true size of the integration horizon, which is the volume of the CFR. Scaling factors, τ_i are introduced to allow the size of the each interval to vary. If the scaled size of each interval is one, then the true total size is the sum of the scale factors for each interval.

The solution methodology is implemented in the software package MINOPT (Schweiger and Floudas, 1997) which is a modeling language and algorithmic framework for mathematical optimization. MINOPT is capable of handling dynamic, time-invariant, and integer variables along with linear, nonlinear, dynamic, and point constraints. Thus MINOPT can address a wide variety of mathematical programming problems including optimal control problems as well as mixed-integer optimal control problems.

COMPUTATIONAL STUDY: METHANE CONVERSION TO ACETYLENE

The proposed approach has been applied to numerous examples ranging from the simpler constant density isothermal and nonisothermal mechanisms involving three reactions to complex nonisothermal mechanisms involving many species and reactions.

This example considers the complex nonisothermal gas phase reaction for the conversion of methane to acetylene. The mechanism involves 36 reactions and 19 species. Hydrogen is provided as a feed along with the methane for use in minimizing the formation of carbon in the reactors. The main products are ethylene, acetylene, hydrogen, and benzene which leads to the formation of carbon. The objective is to maximize the production of acetylene while minimizing the production of benzene.

The reaction mechanism and kinetic constants are taken from Olsvik et al. (1995). The reaction takes place in the gas phase and ideal gas assumptions are made with the pressure constant at 1 atm. All of the kinetic and thermodynamic data for the problem are obtained through a connection to the Chemkin package (Kee et al., 1996). The desired mass fraction of acetylene in the product stream is 0.7 and the mass fractions of the other products are to be minimized. This is reflected in the following objective function:

$$
\begin{aligned}
&1000(y_{\mathrm{C_2H_2}} - 0.7)^2 + 7(y_{\mathrm{CH_2CHCCH}})^2 \\
&+5(y_{\mathrm{C_4H_6}})^2 + 10(y_{\mathrm{C_6H_6}})^2
\end{aligned}
$$

The optimal solution is found to be a CFR with hydrogen fed both to the main feed and along the side of the reactor as shown in Figure 2. The feed temperature is constrained to be less than 1300°K. Since high temperatures are required for any significant conversion, a sharply rising temperature profile is required as shown in Figure 3. The composition profiles are shown in Figure 4.

CONCLUSIONS

The reactor network synthesis problem has been addressed by using a superstructure consisting of CSTR and CFR units. The proposed approach has a sufficiently rich representation of alternatives yet the differential modeling leads to a relatively simple model formulation in comparison to previous superstructure based approaches. The resulting optimal control formulation is solved using control parameterization technique in which the DAEs are integrated explicitly and no approximation is made.

The example problem demonstrates the generality of the approach and the improved results over previous work demonstrates the effectiveness of the overall methodology. MINOPT provides an excellent framework for the modeling and solution of the problem as well as the interpretation of the results.

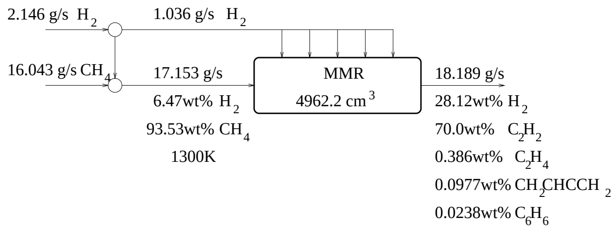

Figure 2. Reactor network solution for the methane conversion example.

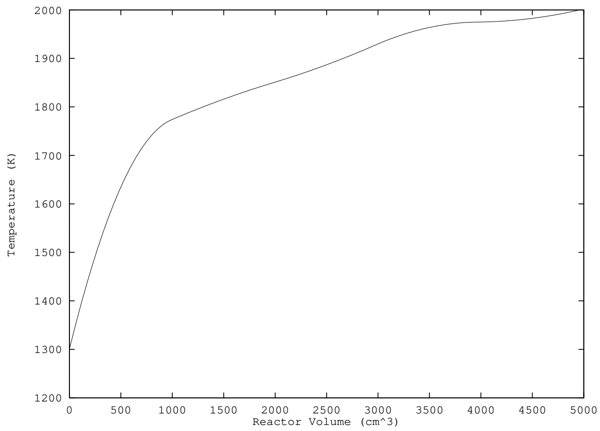

Figure 3. Temperature profiles for the methane conversion solution.

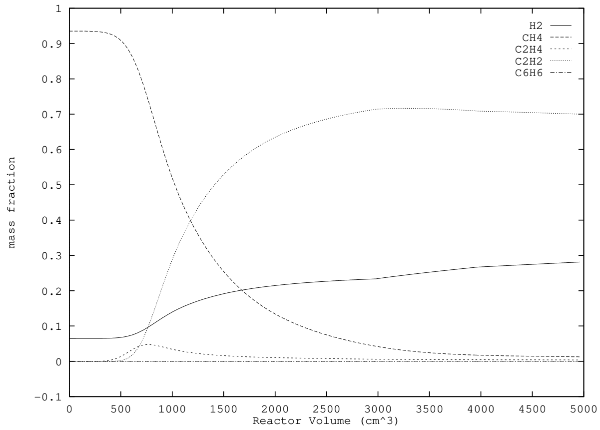

Figure 4. Composition profiles for the methane conversion solution.

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