Physically Feasible Modeling and Simulation of Chemical Processes

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Root finding
Constrained non-linear equations
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The performance of algorithms for solving constrained systems of non-linear algebraic equations is investigated with the objective of developing a method, which can converge to a feasible solution even in presence of discontinuities in the functions, without requiring user intervention. Using as an example a CSTR model, it is demonstrated that certain types of problems can be very difficult to solve using purely numerical algorithms. Symbolic manipulation of the equations may be required to remove the discontinuities from the feasible region in order to alleviate the numerical solution process.

Introduction

Mathematical models of chemical processes may occasionally yield physically infeasible solutions. Typical examples include a fractional conversion factor that is greater than one, or concentration of a component which is negative in a chemical reactor, negative value of the compressibility factor when using a cubic equation of state and temperature crossover in a heat exchanger. Although such solutions do satisfy the mathematical model being used, the results indicate that the model is used outside of its region of validity. In a simulation environment, where the solution of the nonlinear algebraic equations can be just one phase of a complex computational scheme, it is important to ensure that the feasible solution is obtained (and/or selected) without users intervention.

It is possible to add constrains to the process models, which will force the variables to stay inside the feasible region. Several algorithms are available that can solve constrained systems of nonlinear algebraic equations: the "constrained' algorithm of Shacham [1], the iterative linear programming (LP) methods of Bullard and Biegler [2] and Wilhelm and Swaney[3] and the multidimensional bisection method of Gupta [4]. The "constrained' algorithm combines the step-length restricted Newton-Raphson method with the Levenberg-Marquard algorithm (when the Jacobian matrix happens to be singular) and with a continuation approach (if no feasible solution is reached) to keep the variables inside the feasible region and eventually reach a solution in this

region. In the iterative LP technique, linear programs are solved that combine local Jacobian and global bounding information to generate search directions that satisfy region feasibility. In the multidimensional bisection method a sequence of one dimensional problems are solved using bisection in order to ensure that the variables stay inside the feasible region.

The successful uses of Shacham's [1] 'constrained' algorithm for simulation problems are widely documented. Lorenzini *et al* [5] carried out simulation of the ethylene-alpha-olefin co-polymerization process using this method. Sarkar and Gupta [6] used this method for steady state simulation of continuous-flow stirred-tank slurry propylene polymerization reactors. Von Bergen et al [7] applied the 'constrained' algorithm for calculating vapor-liquid equilibrium and density of complex mixtures using the lattice fluid model equations of state. Three most recent applications of this method include simulation of polymer absorption at the solid liquid interface by a continuum model (Juvekar *et al* [8]), simulation of micro-phase enhanced reactions (Hasnat and Roy [9]) and modelling the acid separation behavior of weak base ion exchange resins (Bhandari *et al*. [10]) .

Shacham's [1] constrained algorithm was implemented in POLYMATH 5.0 (POLYMATH is copyrighted by M. Shacham, M.B. Cutlip and M. Elly, http://www.polymath-software.com) numerical computation package and has been used extensively for simulation of various processes (see, for example, Shacham *et al* [11]). We have noticed that the algorithm may occasionally fail to reach a feasible solution and user intervention is needed to enable it to converge (after rearranging the equations, for example). User intervention may not be a viable approach, especially if large-scale problems are concerned. Therefore, to improve the algorithm's performance it is important to identify the reasons for its failure.

In this paper an example is presented where the 'constrained' algorithm (as well as all the other algorithms tested) failed to reach the solution using the basic formulation of the equation set. The reason for the failure is analyzed and possible ways for improving the algorithm are discussed.

An example - consecutive reactions in a CSTR (Fogler [12])

The description of the model equations and the output variables for the example are shown in (tab. 1). The equations represent material and energy balances on a CSTR operating at steady state, in which the consecutive reactions 2A+B->3C, C+2B->D and D->E are carried out. The first five equations are material balance equations (see the "Model Equations' column in (tab. 1)) on species A, B, C, D and E, respectively. These are implicit equations which should be zero at the solution. The sixth equation is also an implicit equation, representing the energy balance on the CSTR. The additional equations are explicit equations, including the Arrhenius expressions for defining the reaction rate coefficients as function of the temperature (8) to (10), definitions of additional terms of the energy balance equation (7) and of

some constants (11) to (13). The equations are shown in a format compatible with POLYMATH 5.0 package, where an "output' variable is selected for every equation (including the implicit equations) for documentation and bookkeeping purposes.

We have attempted to solve this system of equations using the 'constrained' algorithm and two "globally convergent' algorithms from the Numerical Recipes book [13]. The latter algorithms combine search for the minimum of the sum of squares of the function values along the direction assigned by Newton's method or Broyden's method. All three algorithms failed to converge to a solution irrespective of the initial guess used.

A solution could be found by the 'constrained' method only after the equations were modified by multiplying equations (1) to (5) by the respective expressions appearing as denominators, thus eliminating in these equations division by the unknowns. Using the initial guesses shown in (tab. 1), the constrained method converged to the following solution: T= 372.7646 K, CA= 0.002666, CB = 0.033464, CC = 0.837066, CD = 3.97E-04 and CE = 0.808538 (all concentrations are in mol/dm^3). The "globally convergent' methods failed to solve the system even in this modified form.

In an attempt to further alleviate the solution of the problem, the variables T and CA were selected as implicit variables. This allows explicit expression of CA using eq. (1), of CC using eq. (3), of CD using eq. (4) and of CE using eq. (5). With this formulation, only two simultaneous equations have to be solved and all three methods converged to the solution (from the initial guess shown in (tab. 1)). Disregarding the constraints an additional, physically infeasible solution was also found when the iteration was started from large values of CB as initial estimates (like CB =1). The infeasible solution found is T= 328.8334, CA= -0.002, CB= -1.65354, CC= 0.001725, CD= 0.004905 and CE= 1.646368.

Discussion and Conclusions

To investigate the reasons for the failure of all the methods tested, with the original problem formulation, one of the functions (f(CD), eq. (4) in (tab. 1)) is plotted versus the temperature in the vicinity of the solution, (fig. 1). It can be seen that the function value changes very sharply over a very small temperature interval. At T = 372.70 K the function value is 350, at T = 372.7646 K the function value is practically zero and at T = 372.79128 K the function value is unbounded as the denominator in eq. (4) approaches zero. Thus, for a temperature difference smaller than 0.04 K (relative change = 0.01 %), the function value goes from zero to infinity.

The major difficulties associated with the solution of this problem in its original formulation can be summarized as follows. 1. There are points and regions where functions are undefined within the physically feasible region. 2. Some of these discontinuities are extremely close to the solution. The question arises whether there

is an existing numerical algorithm that can successfully deal with such difficulties and, if not, whether such an algorithm can be developed.

The iterative LP ([2] and [3]) and the "multidimensional bisection' [4] algorithms are not suitable for solving this example, because both methods assume function continuity inside the feasible region. In general, all methods that assume function (and derivative) continuity are due to fail for the same reason. Minimum seeking methods, which do not necessarily require continuous functions (such as Powel's method of search, see reference [13], for example), are unsuitable because of the extremely high resolution needed in the line search in order to locate the minimum between two very high function values. Moreover, no convergence to the global minimum can be assured.

Based on the example presented, it seems that the viable approach to solve similar problems is to remove the discontinuities in the feasible region by elimination of the denominators containing unknowns from the equations. This is a simple task for the small-scale example as presented here. However, for large systems of equations and/or more complicated expressions, this could be a rather complicated task. To eliminate discontinuities in the feasible region, without relying on user intervention, a symbolic manipulation program that carries out this task has to be developed.

Table 1: Model Equations and Output Variable Description for the Example

Output variable				
No.	Name	Definition	Initial estimate	Model Equations - Consecutive Reactions in a CSTR |POLVER05_3
1	CA	Concentration of reactant A (mol/dm^3)	CA(0)=.5	f(CA) = V - vo*(CAO-CA)/(2*k1B*CA*CB) #
2	CB	Concentration of reactant B (mol/dm^3)	CB(0)=.01	f(CB) = V - vo*(CBO-CB)/(k1B*CA*CB+2*(k2C*CC*CB^2)) #
3	CC	Concentration of product C (mol/dm^3)	CC(0)=1	f(CC) = V - vo*CC/(3*(k1B*CA*CB) - k2C*CC*CB^2) #
4	CD	Concentration of product D(mol/dm^3)	CD(0)=.01	f(CD) = V- vo*CD/(-k3E*CD + k2C*CC*CB^2) #
5	CE	Concentration of product D (mol/dm^3)	CE(0)=1	f(CE) = V - vo*CE/k3E*CD #
6	T	Temperature in the reactor (K)	T(0)=420	f(T) = 5000*(350-T) - 25*(20+40)*(T-300) + V*SRH #
7	SRH	Heat of reaction (cal/s)		SRH = (2*k1B*CA*CB)*20000 - 2*k2C*CC*CB^2*10000 + 5000*k3E*CD #

8	k1B	Reaction rate coefficient, 1st react (dm^3/mol-s)	k1B = 0.4*exp((20000/R)*(1/300-1/T)) #
9	k2C	Reaction rate coefficient, 2nd react (dm^6/mol^2-s)	k2C = 10*exp((5000/R)*(1/310-1/T)) #
10	k3E	Reaction rate coefficient, 3rd react (1/s)	k3E = 10*exp((10000/R)*(1/320-1/T)) #
11	R	Gas constant (cal/mol*K)	R = 1.987 #
12	V	Reactor volume (dm^3)	V = 500 #
13	vo	Feed flow rate (dm^3/s)	vo = 75/3.3 #
14	CAO	Concentration of A in the feed (mol/dm3)	CAO = 25/vo #
15	CBO	Concentration of B in the feed (mol/dm3)	CBO = 50/vo #

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