

A Non-linear Programming Formulation for Optimal Design and Operation of a Multitubular Packed-Bed Reactor Using a One Stage Solution Strategy (simultaneous solution): Case Study of *o*-xylene Oxidation to Phthalic Anhydride

Carlos A. Llinás Vargas

Chemical Engineering graduate student, Universidad de los Andes, Bogotá, Colombia

Jorge M. Gómez Ramírez

Chemical Engineer, M.Sc, PhD, Professor at Universidad de los Andes, Bogotá, Colombia

ABSTRACT: A one-dimensional pseudo-homogeneous model is used for simulation and subsequent optimization of a MPBR. The reactive system chosen for the present study is Finlayson extended *o*-xylene oxidation to phthalic anhydride production in the presence of undesired side reactions. The case study is actually taken from Froment and Bischoff and in the present article the optimal design and operation of the reactor is searched upon. All programmed simulations and optimizations were achieved by means of Wolfram Mathematica 6.0[®]. As is usual for the present case, sensitivity analyses are done for *o*-xylene inlet concentration (molar fraction) and reactor inlet temperature. The problem for optimization with differential equation constraints is also discussed and several objective functions, technical and economical ones, are maximized.

1 INTRODUCTION

O-xylene oxidation to phthalic has been studied widely and rigorous two-dimensional pseudo-homogenous models have been applied by many [1, 2]. Yet optimal design and operation of such reactor has never been discussed. Though the present article studies the latter the main goal of the case study is actually to formulate a one stage solution strategy for optimization with differential equations as constraints. For such reasons the author admonishes *a priori* any attempt to search for actual optimal design of the reactor at industrial scale in the present article. One has to remember that actual optimal reactor design and operation must be accompanied with pilot plant studies and thoroughly experimental designs. On the other hand kinetic rate law determination through rigorous experimentation and statistics [3] becomes essential when evaluating chemical reactor performance and design even though literature may provide some information on reaction kinetics.

It is then by these means that an already proposed kinetic rate law of pseudo-first order is used in all simulations and no attempt is done for experimental corroboration of the mechanism proposed. Yet simulations with typical system's parameters are run in order

to confirm that the results are physically coherent. Likewise reactor profiles are exhibited for different reactor lengths in such a way that becomes suitable for analysis.

Finally, all simulations and optimizations are done working with a steady state model. All modeling, simulation and optimization was programmed in Wolfram Mathematica 6.0[®] which becomes a convenient software package for solving complex system of differential equations (ODE, PDE, DAE) and optimization problems with already "Built-In Functions". As will be seen the optimization problem with differential equation constraints doesn't become a trivial problem when analytical solutions to such are lacked.

2 MATHEMATICAL MODELING OF FIXED BED REACTORS

When it comes to generalizing the mathematical models for fixed bed reactors, "...it is not possible to concentrate on specific cases and processes. Instead [one must] discuss general models and principles involved in the design and analysis of any type of fixed bed reactor, no matter what process" [1]. The required degree of sophistication in the mathematical modeling is subject in the first place on the process, more specifically on

the sensitivity to perturbations in the operating conditions. Yet of equal importance is the degree of accuracy with which the kinetic and transport phenomena parameters are known.

When it comes to modeling fixed bed reactors probably the most important characteristic of the model is whether it considers the presence of the solid catalyst or not, that is, if a pseudo-homogeneous or heterogeneous model is used. These are usually considered as the two broad categories in fixed bed reactor design. Moreover axial and radial dispersion of mass and energy in either model may be inserted. Yet in the present case axial and radial effects were omitted because the main goal of the one stage solution required the already complex discretization of several differential equations and the solution of these in the optimization problem. Having not neglected such effects would have given rise to new complexities which fall beyond the scope of the present work.

Therefore in the present work a pseudo-homogeneous model without either axial or radial dispersion but variable coolant agent temperature is used. The case study involved 3 reactions, the desired one and two undesired reactions which take place one parallel and the other in series. Solutions to the optimization problems were studied under two scenarios; one in which the desired reaction was only considered and one in which all reactions were taken into account. For such reason the resulting ODE for both cases are shown subsequently.

For the model in which only the desired reaction is studied the resulting ODE's arise from mass balance of the limiting reactant expressed in terms of conversion and energy balance over the reactor and coolant agent. Thus three dependent variables result:

$$\frac{dX}{dz} = \frac{r_1}{v} \quad (1)$$

$$\frac{dT}{dz} = \frac{r_1 H_1 + r_2 H_2 + r_3 H_3 - U(T - T_c)}{v C_p} \quad (2)$$

$$\frac{dT_c}{dz} = \frac{U(T - T_c)}{v_c C_{p,c}} \quad (3)$$

For the model in which all reactions are taken into account the resulting ODE's consist of the mass balance from the 5 species present in the reacting system and the energy balance over the reactor and coolant agent:

$$\frac{dA}{dz} = (r_1 + r_2) \rho_b A_c \quad (4)$$

$$\frac{dB}{dz} = (3r_1 + r_2 + r_3) \rho_b A_c \quad (5)$$

$$\frac{dC}{dz} = (r_1 + r_2) \rho_b A_c \quad (6)$$

$$\frac{dT}{dz} = (-3r_1 - 2r_2 - 5r_3) \rho_b A_c \quad (7)$$

$$\frac{dT_c}{dz} = (-8r_2 - 8r_3) \rho_b A_c \quad (8)$$

$$\frac{dT_c}{dz} = \frac{U(T - T_c)}{v_c C_{p,c}} \quad (9)$$

$$\frac{dT}{dz} = \frac{r_1 H_1 + r_2 H_2 + r_3 H_3 - U(T - T_c)}{v C_p} \quad (10)$$

3 THE OPTIMIZATION PROBLEM

The formulation of an optimization problem consists mainly of three elements: the objective function, the constraints, and the optimization variables or decision variables.

3.1 Objective functions

Three objective functions were maximized in the present article: (1) conversion of o-xylene, (2) production of phthalic anhydride and (3) reactor profitability.

For the optimizations where only optimal operation of the reactor was studied the following objective functions were formulated:

Maximization of o-xylene conversion in the absence of undesired reactions:

$$(1) \text{Maximize } X_{max}$$

Maximization of phthalic anhydride production in the presence of undesired reactions:

$$(2) \text{Maximize } PC_{max}$$

Maximization of reactor profitability in the presence of undesired reactions:

(3) Maximize $\left(\frac{V}{SSR} \left(\frac{FE_{1000} (m.w.FE) (841)}{1000} \right) \right)$ reactor and coolant agent were taken as optimization variables.

On the other hand for the optimization problems where optimal operation and design is search upon simultaneously, the following objective functions were formulated:

Maximization of phthalic anhydride production in the presence of undesired reactions:

(1) Maximize $FC_{maximize}$

Maximization of reactor profitability in the presence of undesired reactions:

(2) Maximize $\left(\frac{V}{SSR} \left(\frac{FE_{1000} (m.w.FE) (841)}{1000} \right) \right)$ in such case the two degrees of freedom turn out to be the inlet temperatures mentioned previously and the reactor length.

3.2 Optimization constraints

The optimization constraints are made up of the model ODE's which lack an analytical solution. Furthermore the following inequality constraints are involved in the optimization problems formulation:

- $0 \leq FA \leq FA_0$ (11)
- $0 \leq FB \leq FB_0$ (12)
- $FC \geq 0$ (13)
- $FD \geq 0$ (14)
- $FE \geq 0$ (15)
- $0 \leq X \leq 1$ (16)
- $T \leq 668$ (17)
- $T_0, T_{c0} \geq 0$ (18)
- $T_0 \leq T$ (19)
- $l \geq 0$ (20)

3.3 Optimization variables

The resulting optimization variables are the dependent variables of the system of ODE's; the o-xylene conversion profile, the molar profiles of the species involved and the reactor and coolant agent temperature profiles. Likewise in order to study the optimal design and operation of the reactor, the reactor length l and the inlet temperatures of the

In the present work results convenient then to divide the optimization problems into two sub-groups: (1) one degree of freedom optimization and (2) two degrees of freedom optimization. The one degree of freedom optimization problems studied uniquely the optimal operation of the reactor, where the degree of freedom resulted in the inlet temperature of the reactor and coolant agent, taken always as equal (i.e. $T_0 = T_{c0}$). On the other hand the two degrees of freedom optimization problems studied the optimal operation and design of the reactor simultaneously.

In such case the two degrees of freedom turn out to be the inlet temperatures mentioned previously and the reactor length.

3.4 Optimization method: One-stage solution strategy

First of all it has to be recognized that the already known optimization techniques are unable to work with ODE as constraints of the optimization problem formulation, that is if it is to be solved simultaneously (one-stage). As the main goal of the present work is to solve the optimization problem in one stage, discretization of the mathematical model turns out to be the first step to take in order to enable a one stage solution. There have been recent proposals mainly in the area of reaction engineer that actually have already encountered the need to use such technique [4].

Most optimization methods work by using first and second derivatives of a Lagrangian function in order to meet the necessary and sufficient conditions of optimality [5]. Accordingly, such local methods of optimization cannot work with differential equations as constraints because their implementation would lead to second and third derivatives which clearly do not represent coherence in optimization techniques. Likewise, global op-

timization methods, though not using derivatives of the constraints to search for optimum, cannot work with differential equations as constraints. Hence a way must be devised by which the pseudo-homogeneous model can be described in analytical terms. Furthermore, an analytical solution of such model is lacked and one must turn to numerical methods to solve it. Clearly optimization with ODE, PDE, DAE constraints is not a trivial problem to solve.

Discretization of mathematical models in order to apply optimization techniques is encountered widely in reaction engineering problems due to the mathematical complexity of these. Numerous methods have been devised to meet such need: Finite differences, finite elements, orthogonal collocation, Rayleigh-Ritz method, etc [6, 7]. Centered finite difference method was used in the case study. In a summarized manner the method simply uses discretization of the dependent variables in n arbitrary collocation points or "mesh". Depending on the mesh size, the number of variables and equations in the model will vary. Clearly as the number of points in the mesh increases computation time increases and the mathematical model becomes bigger. In the present study some optimizations were run with a 50 points mesh and others with a 100 points mesh. Yet is important to mention that results were independent of such parameter and that computation time didn't exceeded 2 minutes in all cases. As an example, the resulting model from the discretization of the reactor temperature can be represented in the following manner:

$$\frac{dT_i}{dt} = f(F_{A_i}, F_{B_i}, F_{C_i}, F_{D_i}, F_{E_i}, T_i, T_{c_i})$$

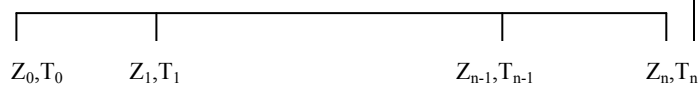


Figure1. Discretization of reactor temperature

$$\text{For } i = \{1, n-1\} \rightarrow \frac{T_{i+1} - T_{i-1}}{2\Delta Z} = f(F_{A_i}, T_{c_i})$$

$$\text{For } i = n \rightarrow \frac{T_{i-1} - T_{i-2}}{\Delta Z} = f(F_{A_i}, T_{c_i})$$

$$\text{where: } \Delta Z = \frac{\text{Reactor length}}{n}$$

From the discretization process it arises that both the number of equality constraints (model) and optimization variables are dependent of the mesh size taken. For the one degree of freedom optimization 100 points were used whereas for the two degrees of freedom optimization a 50 points mesh size was used.

Hence one has from the discretization process mentioned that the actual optimization constraints are the resulting highly nonlinear equations from the discretization of the n conversions, n reactor temperatures, n coolant agent temperatures and n molar flows, n been the number of collocation points (mesh size). Likewise, the resulting optimization variables are each of the mesh points from the discretization of the dependent variables (i.e. $FA_i, FB_i, FC_i, FD_i, FE_i, X_i, T_i, Ta_i$) which exhibit up as will be seen as discrete reactor profiles, plus the degrees of freedom. In tables 1 and 2 the resulting optimization problems formulation are summarized.

Table 1. One degree of freedom optimizations

Objective function	Mesh size	Number of equations	Number of variables	Number of inequality constraints
Maximization o-xylene conversion	100	300	301	301
Maximization phthalic anhydride production	100	700	701	701
Maximization profitability	100	700	701	701

Table 2. Two degrees of freedom optimizations

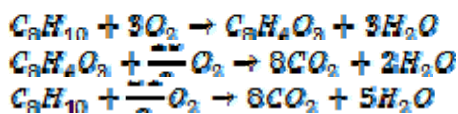
Objective function	Mesh size	Number of equations	Number of variables	Number of inequality constraints
Maximization phthalic anhydride production	50	350	352	352
Maximization profitability	50	350	352	352

3.5 Optimization technique and software

Interior point method was used for all optimizations. The algorithm for such optimization technique is already programmed as a "Built-In Function" in the simulation software Wolfram Mathematica 6.0[®]. That means that the optimization technique, either local or global, can be easily called for by a simple programming line. In the present study for the one stage solution strategy only the interior point method was used because global optimization techniques led to difficulties in computation time. Though a trickier programming was needed for global optimization, global optimization techniques (i.e. Nelder-Mead, Differential Evolution, and Genetic Algorithm) were easily called for in a two level solution strategy. Furthermore it is important to remember that the main purpose of the present study was to formulate a simultaneous solution (one stage solution strategy). Results by both means led to the same solution.

4 CASE STUDY: O-XYLENE OXIDATION FOR PHTHALIC ANHYDRIDE PRODUCTION

The reaction system studied is the oxidation of o-xylene in the presence of undesired reactions [2]:



The reactor usually consists of 2500 tubes up to 10,000 tubes. The length of the tubes is 3 m and their internal diameter is 1 inch. The reaction is carried out over V₂O₅ catalyst and due to selectivity and deactivation problems reactor temperature should not exceed 668K (415°C). A heat transfer medium consisting

of sodium nitrite-potassium nitrate fused salts circulates outside the tubes through the shell to remove the heat of reaction [8]. In the present study as in others the reactor is considered to operate at 1.0 atm, that is, pressure drop is neglected.

Due to the large excess of oxygen at reactor entrance (mole fraction > 0.99), the rate law is considered pseudo first order yet in the present study variations for the oxygen partial pressure was considered. The reaction kinetics and specific reaction rate are taken from [2]:

$$r_1' = -k_1 P_{oxy} P_{O_2} \quad (21)$$

$$r_2' = -k_2 P_{oxy} P_{O_2} \quad (22)$$

$$r_3' = -k_3 P_{oxy} P_{O_2} \quad (23)$$

$$k_1 = \exp\left(19.837 - \frac{10000}{T}\right) \quad (24)$$

$$k_2 = \exp\left(20.86 - \frac{10000}{T}\right) \quad (25)$$

$$k_3 = \exp\left(18.97 - \frac{10000}{T}\right) \quad (26)$$

Where partial pressures are in bars and the subscripts oxy, O₂, pa corresponds to the partial pressures of o-xylene, oxygen and phthalic anhydride respectively.

Given that the undesired reactions are favored at higher temperatures, the inlet reactor and coolant agent temperatures become interesting optimization variables. Similarly, due to the presence of a series reaction the reactor length becomes another interesting optimization variable.

5 RESULTS

Initial results from simulations with typical parameters are exhibited first. Sensitivity analysis is done for reactor inlet conditions, mainly reactor inlet temperature and inlet o-

xylene molar fraction. Afterwards results from the one stage optimizations are shown as discrete reactor profiles.

5.1 Simulation results

For initial simulation of the model certain parameters were taken from the literature [1, 2], others were calculated (i.e. heat capacities), and yet others were changed arbitrarily. Integration of the set of ordinary differential equations was done for a reactor length of 4 m for a better understanding of the reactor profiles. The simulation involved all of three reactions. The study of the system in the absence of undesired reactions was only taken under the optimization section. All parameters used in the study correspond to those of a 2500 tube reactor

Table 3. Parameters for simulation

Parameter	Value
r (m)	0.0127
FT_0 (kmol/s)	0.0006057
yA_0	0.00224
yB_0	0.99776
T_0 (K)	628
T_{a0} (K)	628
P_1 (Pa)	101325
Φ	0.45
ρ_c (kg/m ³)	2800
U (Kj/m ² s K)	0.0845
R_1 (m ³ Pa/ mol K)	8.314
C_{pA} (Kj/kmol K)	244.53
C_{pB} (Kj/kmol K)	32.6
C_{pC} (Kj/kmol K)	238.17
C_{pD} (Kj/kmol K)	36.837
C_{pE} (Kj/kmol K)	48.144
C_{pA} (Kj/kmol K)	1527.769
m(kg/s)	0.04
ΔH_{RX1} (Kj/kmol)	-1285000
ΔH_{RX2} (Kj/kmol)	-3279000
ΔH_{RX3} (Kj/kmol)	-4564000

Illustrations 1, 2 and 3 show the reactor temperature profile, molar profiles and molar profile of the desired product respectively for a 4 m reactor.

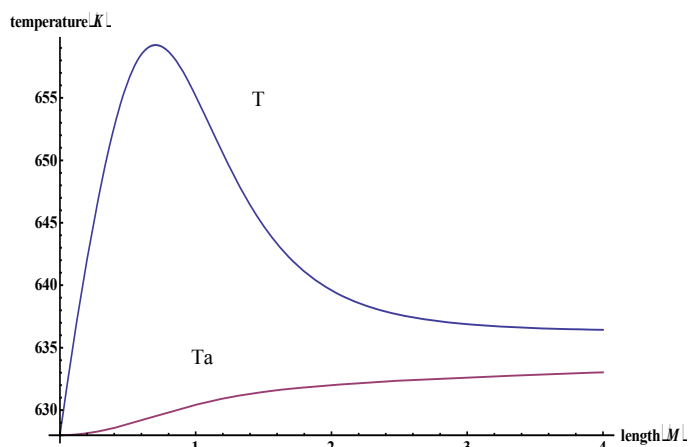


Illustration 1. Reactor temperature profiles

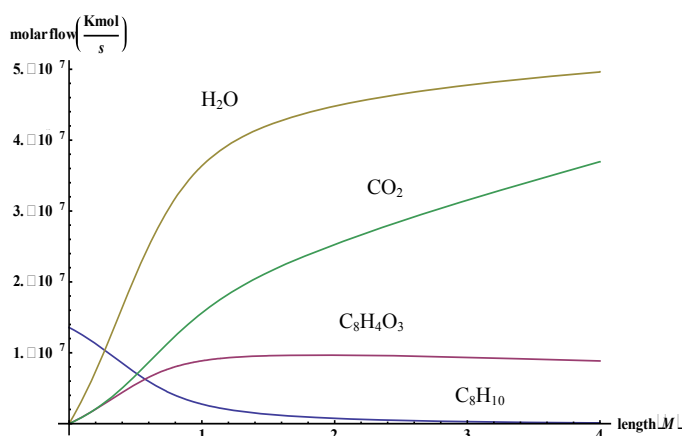


Illustration 2. Reactor molar flow profiles

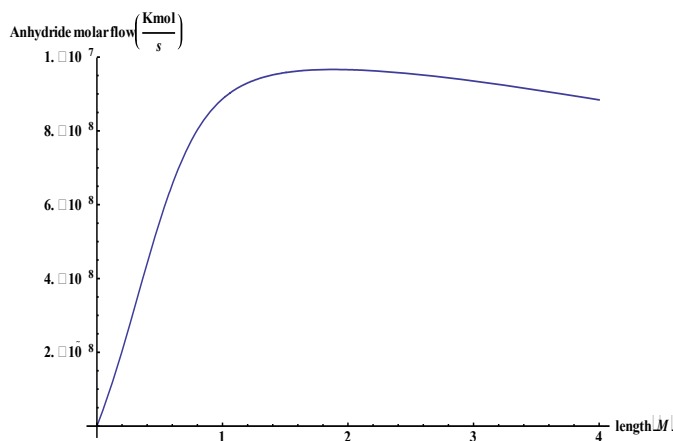


Illustration 3. Phthalic Anhydride molar flow profile

As one may see the reactor exhibits its typical hot spot whose magnitude is function mainly of *o*-xylene inlet concentration and reactor inlet temperature and its location mainly on flow velocity. For the parameters in

the table one may appreciate likewise that side reactions strongly affect reactor performance beyond 2 meters. Thus reactor length becomes an important decision variable to optimize as side reactions are wanted to be kept at a minimum.

5.2 Results for sensitivity to inlet conditions: Sensitivity analysis

For the sensitivity analysis all parameters from the simulation remain the same except that one for which analysis is been done. In the present case sensitivity to changes in reactor inlet temperature and o-xylene inlet molar fraction was performed.

As mentioned previously for the case study, reactor performance is strongly dependent on reactor inlet temperature and concentration. As shown in illustration 4 reactor hot spot and run away ignition starts approximately when inlet temperature is 655K. Likewise as argued initially the idea of operating such reactor over 668K becomes unacceptable thus reactor inlet temperature clearly becomes an optimization variable.

Similarly, sensitivity to o-xylene inlet molar fraction is show in illustration 5. Run away reaction is also evident when inlet molar fraction reaches up to 0.0032. Such strong hot spots clearly affect catalyst performance and lifetime. In the present case study is clear then that a thermal runaway limit exists and its prediction becomes important if one desires to avoid reactor sensitivity. Molar fraction value for the first entrance condition is now shown on illustration 5. Its corresponding value is 0.001.

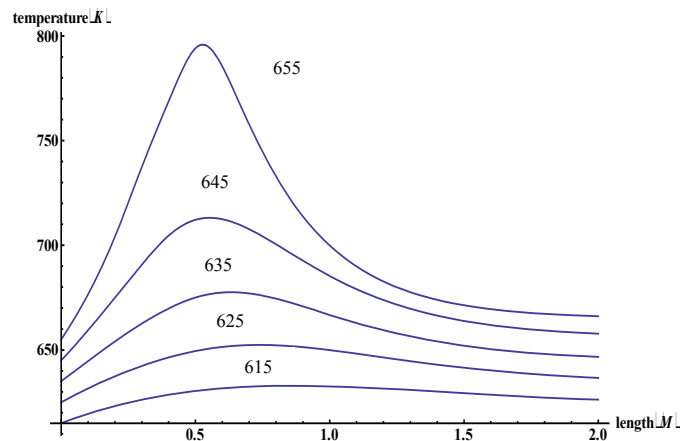


Illustration 4. Sensitivity to inlet reactor temperature

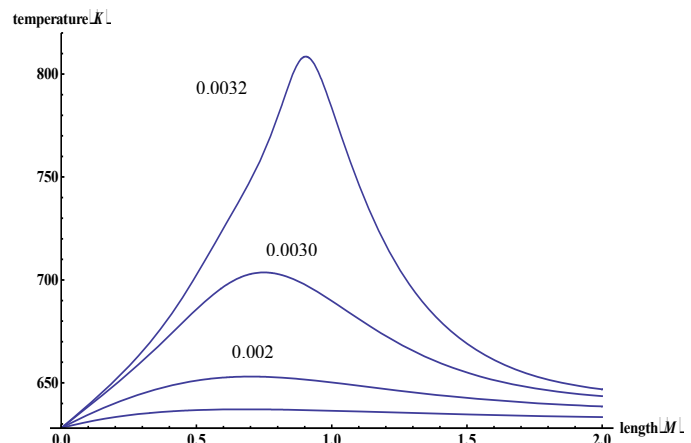


Illustration 5. Sensitivity to o-xylene inlet molar fraction

Thermal runaway limit actually may be defined at the inflection point of the temperature profile. Such problem may be visualized quantitatively under a strict mathematical perspective. It is this what actually Shahid Bashir et al. do as they prove that to avoid thermal runaway in cooled reactors the second derivative of the reaction temperature along the tube length must remain less than zero[9]:

$$\frac{d^2T}{dz^2} \leq 0$$

(27)

Moreover they emphasize that the cause for a temperature runaway is that the $\frac{d^2T}{dz^2}=0$ limit is exceeded. It is evident for the present reactive system under study that such limit has already been exceeded when the inlet molar fraction is 0.0032 (i.e. a change in concavity has already occurred).

On the other hand, for the inlet temperature sensitivity, it seems as if the threshold value for reaction thermal runaway were slightly less than 655K. A small change in concavity is weakly appreciated at the beginning of the temperature profile for the latter inlet temperature indicating that the second derivative criterion has already been violated.

5.3 Optimization results

For the optimization problems all parameters from table 3 remained the same except the *o*-xylene inlet molar fraction which was parameterized to 0.003 and the inlet temperatures (i.e. T_0 , T_{a0}) which were taken always as optimization variables and equalized. For the optimizations which studied only the optimal operation of the reactor (i.e. one degree of freedom), that is, where the length of the reactor is a parameter, a 2 meter reactor was assumed. Tables 4 and 5 summarize the optimization results:

Table 4. One degree of freedom optimization results: Inlet temperature

Objective function	Optimal inlet temperature(K)	Maximum reactor temperature attained(K)	Objective function value
Maximization <i>o</i> -xylene conversion	624.83	668	0.941475
Maximization phthalic anhydride production	617.88	657	0.46738 mol/hr
Maximization profitability	613.97	643	0.468689 \$/hr

Table 5. Two degrees of freedom optimization results: Inlet temperature and reactor length

Objective function	Optimal reactor length(m)	Optimal inlet temperature(K)	Maximum reactor temperature attained(K)	Objective function value
Maximization phthalic anhydride production	3	613.874	645	0.47313 1 mol/hr
Maximization profitability	2.4	611.119	637.8	0.44747 9 \$/hr

In what follows sub-optimal temperature profiles result from simulations where system constraints are intentionally violated, mainly the maximum allowable temperature, are shown. After each sub-optimal profile optimal profiles result from the optimizations are illustrated. It remains important to emphasize that different optimal criteria led to different outcomes in the optimal design and operation of the reactor.

Maximization *o*-xylene conversion:

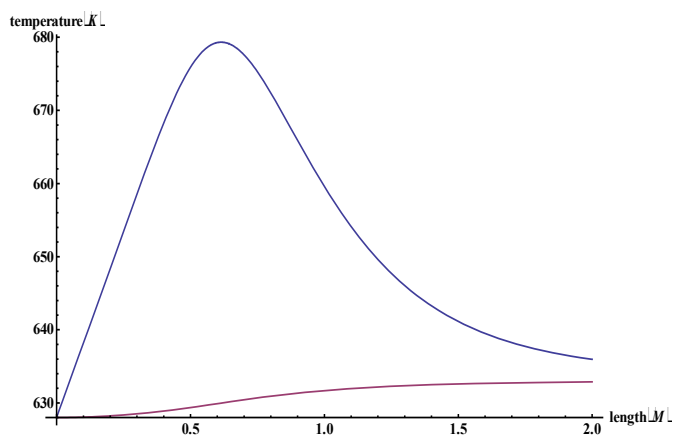


Illustration 6. Initial sub-optimal temperature profile

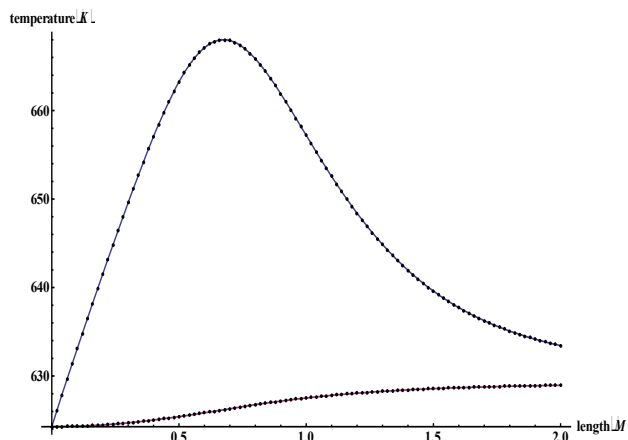


Illustration 7. Final optimal temperature profile

Maximization phthalic anhydride production (1 degree of freedom):

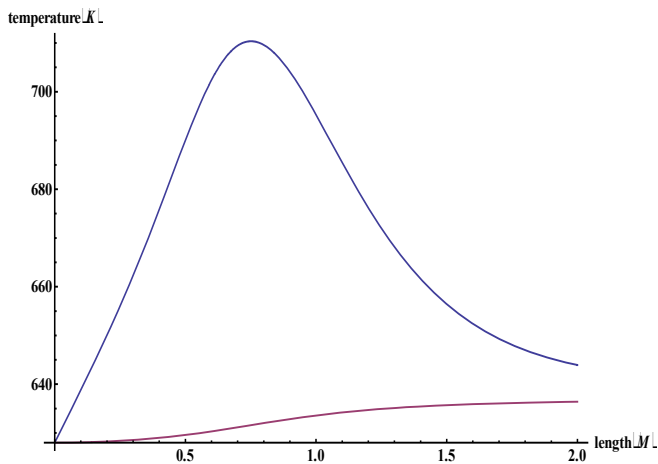


Illustration 8. Initial sub-optimal temperature profile

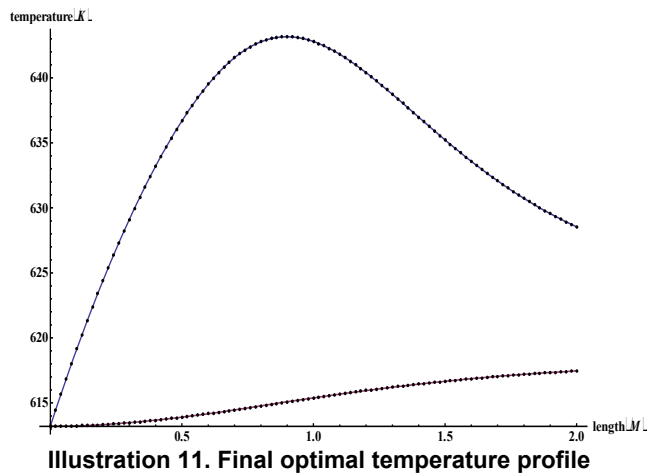


Illustration 11. Final optimal temperature profile

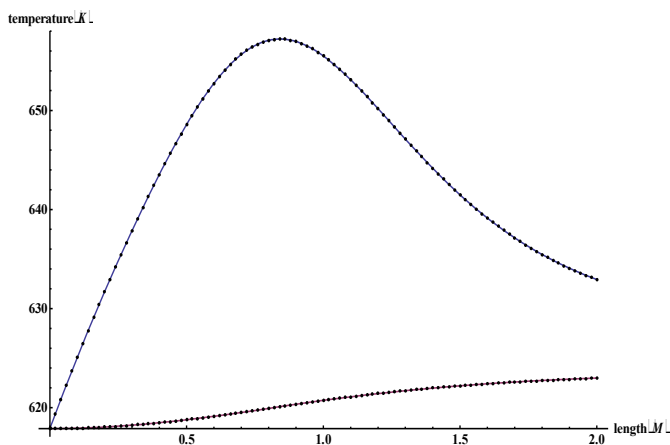


Illustration 9. Final optimal temperature profile

Maximization reactor profitability (1 degree of freedom):

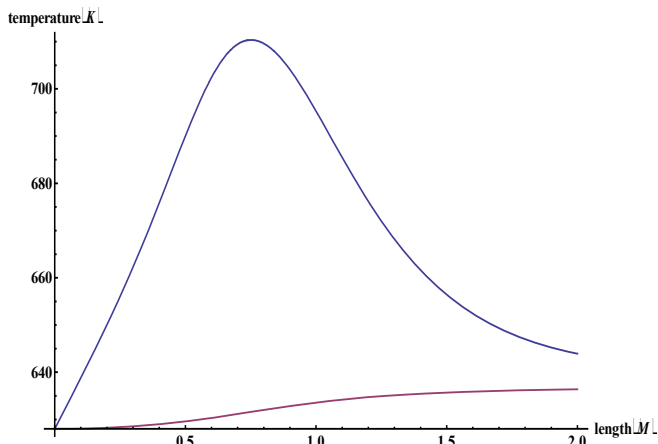


Illustration 10. Initial sub-optimal temperature profile

The molar flow profiles for the production of the desired product (i.e. phthalic anhydride) behaved quite the same in all optimizations. Illustrations 12 and 13 show the sub-optimal and optimal molar flow profile for phthalic anhydride respectively. The illustrations were taken from the maximization of the reactor profitability with one degree of freedom:

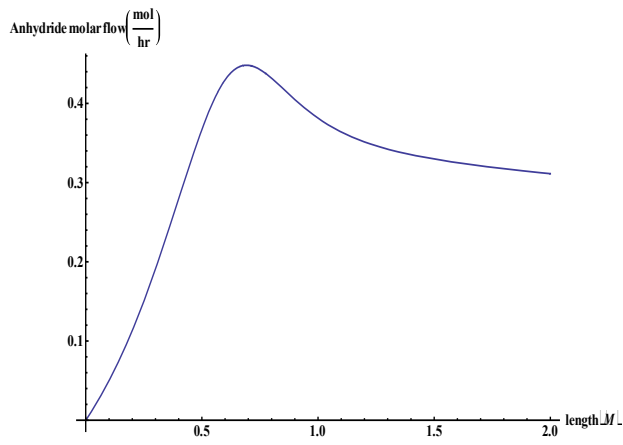


Illustration 12. Initial sub-optimal phthalic anhydride molar flow profile

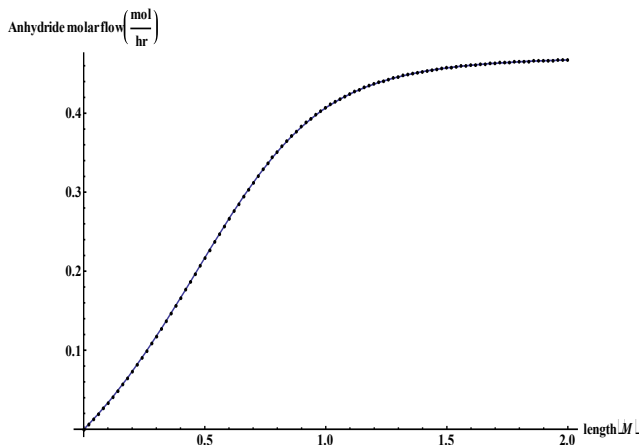


Illustration 13. Final optimal phthalic anhydride molar flow profile

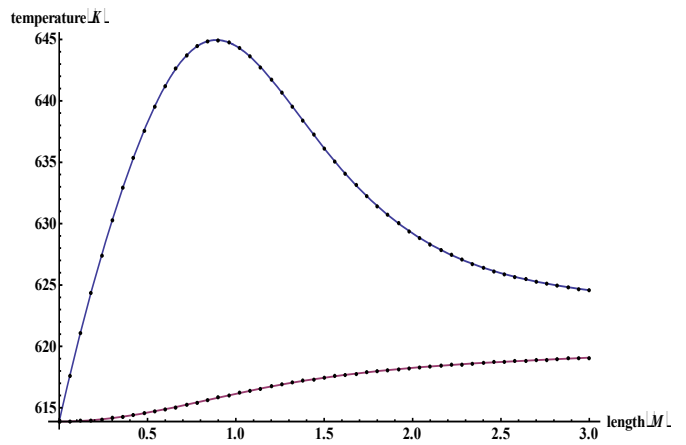


Illustration 15. Final optimal temperature profile

Maximization reactor profitability (2 degrees of freedom):

Maximization phthalic anhydride production (2 degrees of freedom):

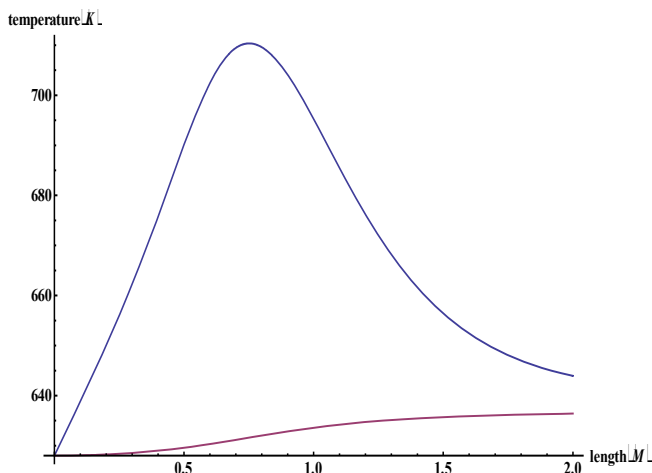


Illustration 14. Initial sub-optimal temperature profile

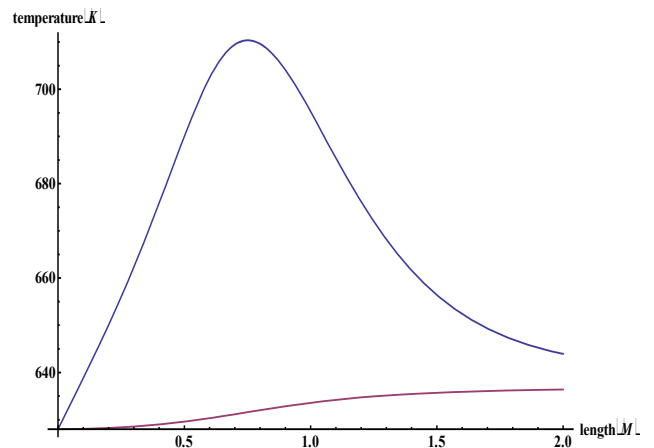


Illustration 16. Initial sub-optimal temperature profile

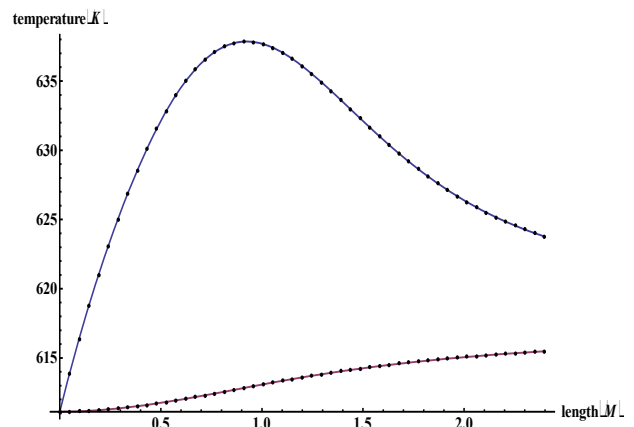


Illustration 17. Final optimal temperature profile

The following illustrations exhibit the initial and final molar flow profiles for the case where maximization the reactor profitability with two degrees of freedom is studied.

Clearly optimal reactor design and operation led to optimal molar flow profiles as phthalic anhydride production is kept at its maximum whilst CO₂ from the undesired reactions is kept at a minimum.

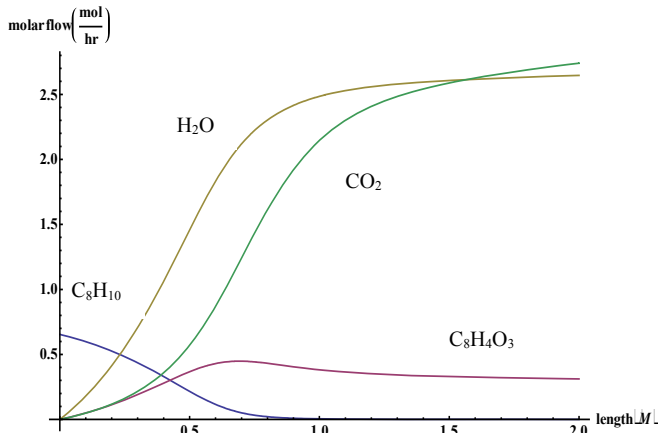


Illustration 18. Initial sub-optimal molar flow profiles

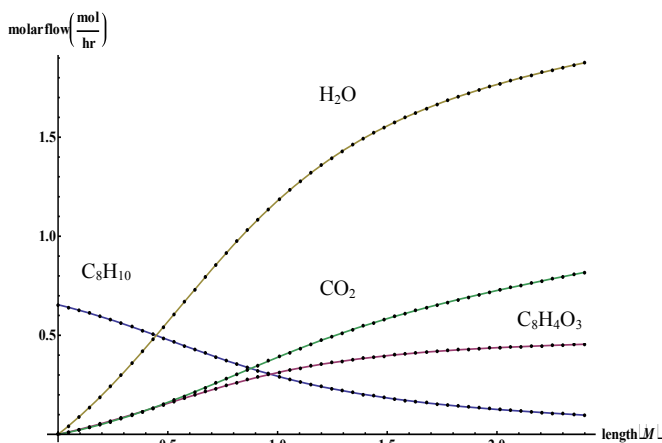


Illustration 19. Final optimal molar flow profiles

Finally a graph of the objective function for the reactor profitability with two degrees of freedom is shown. By using the results from the profit objective function, one may insert the result for inlet optimal temperature (i.e. 611.119K) in a one degree of freedom optimization and obtain a graph of profit as a function of reactor length. Notice that a maximum is attained when reactor length is approximately 2.4m. Hence by reducing the reactor profit optimization from two degrees to a one degree of freedom optimization and inserting the optimal inlet temperature from the two degrees of freedom case, the graph

bolsters the result obtained from the two degree of freedom optimization.

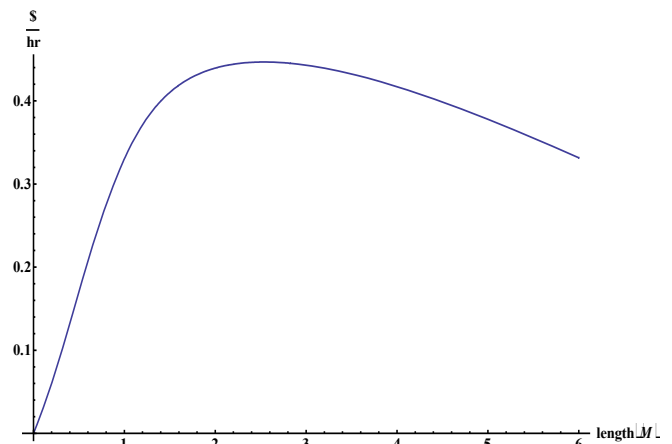


Figure 18. Objective function maximum

6 CONCLUSIONS.

Reactor simulation for phthalic anhydride production was done for some typical parameters. Reactor sensitivity analysis for inlet temperature and *o*-xylene inlet concentration was done in order to pinpoint reaction thermal runaway limit. The concavity criterion showed to be right for the present case as an unacceptable temperature of 800K exhibited when change in concavity of the profiles took place.

Optimization led to minimization of the problems of selectivity in the reactive system, mainly the presence of the side reactions. Moreover such minimization of side reactions was accomplished by maintaining the temperature below its constrained value, 668K. While the one degree of freedom problems solved the optimal operation of the reactor, two degrees of freedom optimizations were able to solve the problem of optimal operation and design simultaneously.

All optimizations kept phthalic anhydride production at a maximum and CO₂ production at a minimum as presented in illustrations 19. The one degree of freedom maximization of the *o*-xylene conversion was the

only case where undesired side reactions were not considered thus leading to the highest optimal inlet temperature. Likewise this case reached the highest hot spot, up to the limit imposed by the inequality constraint (i.e. $T \leq 668K$).

The problem of optimization with differential equations that lack an analytical solution was solved by discretization of the mathematical model and using a one level solution strategy. Centered finite difference was used to discrete the mathematical model. Solution of the optimization problem was seen to be independent of the mesh size used yet computation time did show dependent of such parameter. Finally optimization results were obtained for reactor inlet temperature and length. Such optimizations led to optimal temperature profiles and molar profiles by keeping production of undesired products to a minimum.

NOTATION

- r_1' = RX 1 kinetic rate law
- r_2' = RX 2 kinetic rate law
- r_3' = RX 3 kinetic rate law
- k_1 = RX 1 specific rate
- k_2 = RX 2 specific rate
- k_3 = RX 3 specific rate
- X = o - xylene conversion
- T = reactor temperature [K]
- T_c = coolant agent temperature [K]
- F_A = o - xylene molar flow
- F_B = O₂ molar flow
- F_C = phthalic anhydride molar flow
- F_D = H₂O molar flow
- F_E = CO₂ molar flow
- r = reactor radius [m]
- A_c = reactor cross sectional area [m²]
- a = heat exchange area per unit reactor volume
- FT_{in} = total inlet molar flow
- yA_0 = o - xylene inlet molar fraction
- yB_0 = O₂ inlet molar fraction
- T_0 = reactor inlet temperature [K]
- T_{c0} = coolant agent inlet temperature [K]
- P = system pressure [Pa]

- ϕ = bed porosity
- ρ_c = catalyst density
- ρ_b = bulk density
- U = overall heat transfer coefficient
- R = ideal gas constant
- Cp_A = o - xylene heat capacity
- Cp_B = O₂ heat capacity
- Cp_C = phthalic anhydride heat capacity
- Cp_D = H₂O heat capacity
- Cp_E = CO₂ heat capacity
- Cp_c = coolant agent heat capacity
- m = coolant agent mass flow
- ΔH_{RX1} = RX1 heat of reaction
- ΔH_{RX2} = RX2 heat of reaction
- ΔH_{RX3} = RX3 heat of reaction
- z = reactor axial coordinate [m]

OPTIMIZATION CONSTANTS NOTATION

- m.w.FC = phthalic anhydride molecular weight
- m.w.FE = CO₂ molecular weight
- p = anhydride price, 9
- pr = reactor cost, 50
- par, ser = weight contribution to lost incomes, 0.5
- w = repayment multiplier, 0.624 [year⁻¹]
- l = reactor length [m]
- 0.301 = parallel reaction stoichiometry
- 1.36 = desired reaction stoichiometry
- 0.41 = series reaction stoichiometry

REFERENCES

- [1] Froment, G.F. and K.B. Bischoff, *Chemical Reactor Analysis and Design*, John Wiley & Sons, New York (1990)
- [2] B. Rosendall and B.A. Finlayson, *Transport Effects in Packed-Bed Oxidation Reactors*, Computers chem. Engng Vol. 19 No. 11 (1995)
- [3] H. Scott Fogler, *Elements of Chemical Reaction Engineering*, Prentice Hall, Fourth Edition (2006)
- [4] Arturo M. Cervantes, Andres Wächter, Reha H. Tütüncü, Lorenz T. Biegler, "A reduced space interior point strategy for optimization of differential algebraic systems",

Computers and Chemical Engineering 24
(2000)

[5] Thomas F. Edgar, David M. Himmelblau,
"Optimization of chemical processes",
McGraw-Hill, Second Edition, (2001)

[6] Finlayson, B. "Nonlinear Analysis of
Chemical Engineering", McGraw-Hill, New
York, (1980)

[7] Richard L. Burden. "Numerical Analysis",
Thomson-Learning, Seventh edition, (2002)

[8] Warren D. Seider, J.D. Seader, Daniel R.
Lewin, "Product and Process Design Prin-
ciples", John Wiley & Sons, Second Edition,
(2004)

[9] Shahid Bashir, Tibor Chován, Bassam J.
Masri, Ananya Mukherjee, Alok Pant, Sumit
Sen, and P. Vijayaraghavan, "Thermal Ru-
naway Limit of Tubular Reactors, Defined at
the Inflection Point of the Temperature Pro-
file", Ind. Eng. Chem. Res, Vol 31, No.9,
(1992)