MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

DYNAMIC OPTIMIZATION OF BATCH AND SEMI-BATCH CHEMICAL PROCESSES

RANA GÜLİZAR ÖZVERİ

MASTER THESIS
Department of Chemical Engineering

Thesis Supervisor
Assoc. Prof. Kurtul KÜÇÜKADA

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Rana Gülizar ÖZVERİ, a Master of Science student of Marmara University Institute for Graduate Studies in Pure and Applied Sciences, defended her thesis entitled "**Dynamic Optimization of Batch and Semi-Batch Chemical Processes**", on June 16, 2016 and has been found to be satisfactory by the jury members.

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APPROVAL

Marmara University Institute for Graduate Studies in Pure and Applied Sciences Executive Committee approves that Rana Gülizar ÖZVERİ be granted the degree of Master of Science in Department of Chemistry, Chemical Engineering Program on 26.08.2016........ (Resolution no: 2016/20-02.........).

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Abstract

THESIS TITLE: DYNAMIC OPTIMIZATION OF BATCH AND SEMI BATCH CHEMICAL PROCESSES

Batch and semi-batch processes are very important and widely used processes in chemical industry. They are used especially in fine chemical industry, including wide variety of chemicals, pharmaceuticals, polymers as in batch processes. When the production volumes are low, the process is realized as an isolated system because of safety and for sterilizing. The batch processes are the techniques to be used when handling of the materials are difficult. Batch operations are processes where the materials are fed to the tank and then no change during the process. Despite batch operations, in semi-batch operations, reactants or products can be removed or added during the process (Bonvin et al, 2003).

Regarding the dynamic nature of batch processes, the problems they reveal in modeling and control, are the most interesting and challenging ones. Most of the chemical engineering processes are operated as continuous processes; however batch processes are performed in specialty chemicals with smaller volume and in pharmaceutical industry. Chemical batch reactors have advantages against continuous reactors where particularly slow rate constants in a continuous reaction come into question (Luyben, 1996).

Semi batch, semi flow or semi continuous processes take place in single stirred tank with equipments very similar to the ones that are used in batch processes. Most of the time, some of the reactants are fed into the tank primarily and the rest is fed gradually. This type of reactant feed has an advantage where there are large heat effects in the reaction and when high reactant concentrations lead to undesirable intermediate products or when some of the reactants are in gas phase which has a limited solubility. Reactor design of semi batch processes is really the difficult part, since it is an open system that operates under nonsteady-state conditions. According to this difficulty, the mass and energy equations for a semi batch process are more complicated than batch or continuous processes (Hill, 1977).

Because of the importance of the batch processes and wide variety of usage, optimization of these kinds of processes is reviewed recently. Optimization of any kind of process means the reduction of production costs, improving product quality,

implementing the needs of safety and environmental requirements and regulations (Bonvin et al, 2002). If we take a look at the industry, the perspective is to minimize the batch cycle time for increasing the profit of the production. The reason for the attention concerning the batch processes in recent years is that batch processes are flexible to adapt in small volume productions (Tan et al, 2012).

It is necessary to determine the operational range (operating conditions of variables) and operation time of the manipulated variables in batch processes in order to maximize the efficiency and minimize the energy consumption or production cost for an efficient operation. Efficiency, energy consumption subjects are considered limitedly about batch processes (Bonvin et al, 2003). Mujtaba et al. studied on increasing the yield of desired product of batch and semi-batch processes. The optimal temperature profile for batch processes and optimal temperature profile and feed for semi-batch processes are examined (Pahija et al, 2014).

In literature, there are many studies on the batch, semi-batch and optimization subjects. However, there are few studies about systematic optimization for batch and semi-batch processes. These few studies consider very simple and batch processes. Thus, in this study, the purpose is to investigate the process by classifying and systematically dividing them into subgroups (sub processes) and develop optimization methods.

For the proposed aim, control vector iteration and trajectory optimization techniques were used in this study. Batch and semi-batch processes were subject to different optimization techniques. While the control of isothermal processes was elementary and easily achievable, the control of non-isothermal processes was challenged to be optimized.

As a consequence, the techniques that are used in this study can be implemented into laboratory scaled processes and then by a distinct control, they can be implemented into large scale industrial processes in order to control the temperature, the yield and also by further and extensive studies, even the cost of the production can be controlled by developing the techniques proposed in this study.

JUNE, 2016 RANA GÜLİZAR ÖZVERİ

Özet

TEZ BAŞLIĞI: KESİKLİ VE YARI KESİKLİ KİMYASAL PROSESLERİN DİNAMİK OPTİMİZASYONU

Kesikli ve yarı kesikli prosesler, kimya endüstrisinde geniş alanlarda kullanılan önemli proseslerdir. Özellikle kimya, ilaç, polimer alanlarında kesikli proses olarak ince kimyasal endüstride kullanılmaktadırlar. Üretim hacimleri düşük olduğunda, proses, güvenlik ve sterilizasyon açısından izole bir sistem olarak kabul edilir. Kesikli prosesler, materyallerin işlenmesi zor olduğunda kullanılan tekniklerdir. Kesikli bir proses, materyaller tanka beslendikten sonra proses boyunca herhangi bir miktar değişimi olmayan prosestir. Kesikli proseslerin aksine, yarı kesikli proseslerde, reaktantlar veya ürünler, proses boyunca eklenebilir veya çıkarılabilir (Bonvin et al, 2003).

Kesikli proseslerin dinamik doğasına bağlı olarak, modelleme ve kontrolde ortaya çıkardıkları problemler en ilginç ve aynı zamanda da en ilgi çekici problemlerdir. Kimya mühendisliğindeki proseslerin bir çoğu sürekli proses olarak gerçekleştirilirken, kesikli prosesler genelde daha küçük hacimli özel kimyasallar ve ilaç endüstrisinde gerçekleştirilir. Bu ürünlerin üretildiği kesikli kimyasal reaktör, düşük hız sabitine sahip sürekli reaktörlere göre avantajlıdır (Luyben, 1996).

Yarı kesikli, yarı akışlı veya yarı sürekli prosesler, kesikli proseslerde kullanılan ekipmanlara çok benzer ekipmanlarla birlikte çalıştırılan tek karıştırmalı tanklarda gerçekleştirilir. Genelde, reaktantlardan bazıları tanka ilk başta eklenir, geriye kalan reaktantlar ise tanka yavaş yavaş eklenir. Böyle bir reaktant beslemesi, reaksiyonda yüksek ısı etkileri olduğunda, yüksek reaktant konsantrasyonları istenmeyen ara ürünleri oluşturduğunda veya sınırlı çözünürlüğe sahip gaz halinde reaktantlar olduğunda avantajlıdır. Yarı kesikli proseslerin reaktör tasarımı da bu doğrultuda, açık bir sistem olması ve kararlı halde olmaması nedeniyle zordur. Bu zorluğa bağlı olarak, yarı kesikli proseslerin kütle ve enerji denklikleri, kesikli veya sürekli proseslerinkine göre daha karışıktır (Hill, 1977).

Kesikli proseslerin önemi ve geniş alanlarda kullanımı, yakın zamanlarda bu proseslerin optimizasyonunu inceleme nedenlerini oluşturmuştur. Herhangi bir prosesin optimizasyonu, üretim maliyetlerinin düşürülmesi, ürün kalitesinin arttırılması, güvenlik ve çevre gerekliliklerinin ve yönetmeliklerinin uygulanması demektir (Bonvin

et al, 2002). Endüstriye bakıldığında, bakış açısı üretimden edilecek kârın arttırılması için seri döngü süresini en aza indirgemektir. Yakın zamanlarda kesikli proseslere yöneltilen bu ilginin nedeni, küçük hacimli üretimlere kolayca adapte olabilmeleridir (Tan et al, 2012).

Verimli bir operasyon için, enerji tüketiminin veya üretim maliyetinin en aza indirgenmesi ve verimliliği en fazla yapabilmek için kesikli proseslerde ayarlanmış değişkenlerin operasyonel aralığı (değişkenlerin çalışma aralığı) ve çalışma süresinin belirlenmesi gereklidir. Verimlilik, enerji tüketimi başlıkları, kesikli prosesler için sınırlı olarak gündemdedir (Bonvin et al, 2003). Bazı çalışmalarda, kesikli ve yarı kesikli proseslerin istenilen ürününün kazancını arttırmak üzerine çalışılmıştır. Bunun yanı sıra, kesikli prosesler için optimum sıcaklı profili ve yarı kesikli prosesler için optimum sıcaklık profili ve beslemesi incelenmiştir (Pahija et al, 2014).

Literatürde kesikli, yarı kesikli ve optimizasyon üzerine bir çok çalışma bulunmaktadır. Ancak, kesikli ve yarı kesikli proseslerin sistematik optimizasyonu için az sayıda çalışma bulunmaktadır. Bu çalışmalar, genel olarak çok basit ve kesikli prosesleri göz önünde bulundurmaktadır. Bu çalışmada amaç, prosesi alt gruplara (alt proseslere) sistematik olarak bölüp sınıflandırarak incelemek ve optimizasyon yöntemleri geliştirmektir.

Önerilen amaç doğrultusunda, kontrol vektör iterasyonu ve yörünge optimizasyonu teknikleri bu çalışmada kullanılmıştır. Kesikli ve yarı kesikli prosesler, farklı optimizasyon tekniklerine konu edilmiştir. İzotermal proseslerin kontrolü basit ve kolay ulaşılabilirken, izotermal olmayan proseslerin kontrolü optimize edilirken zorluklarla karşılaşılmıştır.

Sonuç olarak, bu çalışmada kullanılan teknikler laboratuvar ölçekli proseslere uygulandıktan sonra düzgün bir kontrolle, sıcaklığı, ürün verimini ve hatta daha ileri ve kapsamlı çalışmalarla, bu çalışmada önerilen tekniklerin geliştirilmesiyle üretim maliyetini geliştirmek üzere büyük ölçekli endüstriyel proseslere uygulanabilir.

HAZİRAN, 2016 RANA GÜLİZAR ÖZVERİ

Symbols

V	Volume
C	Concentration
C_A	Concentration of A
C_{Ao}	Initial concentration of A
C_R	Concentration of R
C_{Ro}	Initial concentration of R
C_S	Concentration of S
C_B	Concentration of B
C_C	Concentration of C
C_D	Concentration of D
t	Time
k_i	Reaction rate constant for reaction i
k_{io}	Arrhenius constant for reaction i
T	Temperature
ρ	Density
T_M	Metal wall temperature
T_j	Jacket temperature
V_j	Volume of the jacket fluid
V_M	Volume of the metal wall
C_M	Specific heat capacity of the metal wall
E	Activation energy
F_w	Cooling water feed
F_s	Steam feed
T^{set}	Set point temperature
W_c	Condensate
V-i	Valve number for valve i
α	Preexponential coefficient
R_{gas}	Universal gas constant
C_p	Spesific heat capacity
H	Enthalpy
A	Area

h	Film coefficient
ΔH	Heat of reaction
ΔG	Gibbs free energy
ΔS	Entropy
υ_o	Volumetric flow rate
V_o	Initial volume in the reactor
T_{eq}	Equilibrium temperature
r	Reaction rate
q	Fluid flow rate
θ	Residence time
n	Reaction order
t_{opt}	Optimal time
e	Exponential
a	Coefficient
b	Coefficient
c	Coefficient
f(x)	Input value
f(c)	Output value
U	Overall heat transfer coefficient
T_a	Temperature profile for control vector iteration
Δt	Time interval
Δx	Distance interval
dH/dT	Hamiltonian differential expression
Y	One dimensional adjoint function
X	Distance dimension
Z	Two dimensional adjoint function
G_1	Best function to optimize the problem
F	Function
Q	Heat removal
N	Mole numbers

Abbreviations

TT	Temperature transmitter
exp	Exponential
EM	Euler’s method
s	Second
NLP	Non-linear programming
Ana	Analytical
Num	Numerical
$_{eq}$	Equilibrium
n^{th}	The last term of a sequence
ODE	Ordinary differential equations
opt	Optimal
Rx	Reaction
SS	Scale space
CVI	Control vector iteration
$_{max}$	Maximum

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Chapter 1

1. Introduction

1.1. Batch Processes in Chemical Engineering

Most of the processes in chemical engineering are tend to be done as continuous processes. Nonetheless, batch processes should not be ignored. Remarkably, for smaller scale processes, batch operations are very suitable (Richardson and Peacock, 1991).

Batch processes are the processes that operate in contrast with continuous processes. In a batch process, product or the materials are fed in discrete amount. Occasionally, this denotes that temperature, mass, concentration, heat and other properties of a process change with time. Generally, batch processes are combinations of batch and semi batch processes. During the semi batch part, the start-ups and shutdowns of the process are applied with a period, while the feed is removed with a pump. In a heat exchanger, feed is heated and in the reactor, heating is continued with a reactor jacket steam heater. Reaction takes place and later on cooling water is sent to the jacket. After the completion of the reaction, product is removed with a pump. Finally, the product that is withdrawn cooled down with a heat exchanger before storing. The first two steps are semi batch. Here, filling the reactor, preheating and the part where pumping into empty reactor and product-cooling parts are semi batch. Later on, reactor heating, reaction that is taking place and cooling with the reactor jacket are all batch processes. Batch processes are economically preferable for small volume productions, flexible processes that can adapt the changes of the product formulation and they allow product identification and using multifunctional standard equipment for producing many types of products within the same plant also if the equipment needs periodic sterilization. In industries, like pharmaceuticals and food, identification of batch products must be done apparently by indicating the production date, feeds and properties, conditions of the process. This is easily achieved by a batch process. Thinking widely, if a problem occurs within a certain batch, that only batch can be withdrawn, not necessarily all of the products on the market. Besides pharmaceuticals and food industry, most of the fine chemicals are produced with batch processing, but the products of these industries are sometimes sensitive for the impurities in the final product. All of the industries mentioned above are batch processes but they also have semi batch steps during the overall process. At the beginning of a batch process, laboratory scaled designs are constructed, which means that the first concern of a batch process differs from the industrial large scale continuous processes. Especially in specialty chemicals industry, delivering the product into the market instantaneously is the main priority. According to this demand, the full process design and other necessities should be done in parallel (Smith, 2005).

Regarding the dynamic nature of batch processes, the problems they reveal in modeling and control, are the most interesting and challenging ones. Most of the chemical engineering processes are operated as continuous processes; however batch processes are performed in specialty chemicals with smaller volume and in pharmaceutical industry. Chemical batch reactors have advantages against continuous reactors where particularly slow rate constants in a continuous reaction come into question. Considering a batch reactor such as in Fig. 1.1, the reactant A is charged into the vessel. The desired temperature is achieved by the steam that is fed into the jacket. However, for maintaining the desired temperature, the jacket is filled with sufficient cooling water.

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

Considering a series of reactions shown as above, A is converted into the desired product, R. Unfortunately, if the reaction is carried out for more time than the limit of exactly the right time and condition, R reacts into the undesired side product S, so the yield of R will be lower than the expected. Conversely, if the reaction carries on for less time than the limit of exactly the right condition, the conversion of A will be low, resulting in low yield of R. Consequently, in such processes, the optimum batch time and processes conditions should be decided. In some processes, the exothermic effect is removed by cooling or there can be an optimum temperature profile for the process. If the specific reaction rates for the consecutive reactions, k_1 and k_2, as much as the activation energies of the relevant equations are the same, then the reaction could be performed at the desired maximum temperature, minimizing the batch time. The maximum temperature could be decided according to maximum operation temperature or pressure of the equipment or even by the process characteristics of the products such as degradation and polymerization where high temperatures are needed (Luyben, 1996).

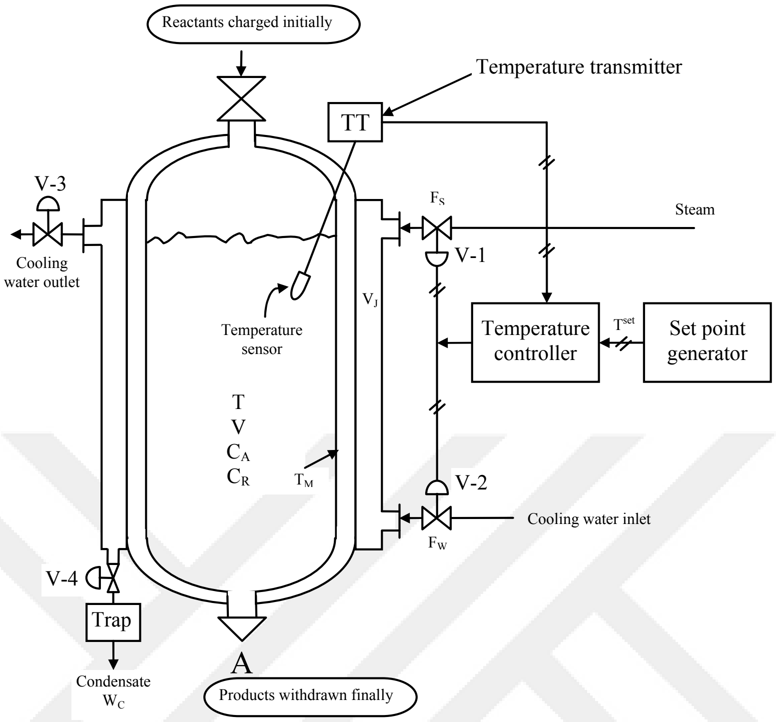


Figure 1.1 Schematic representation of a batch reactor.

If k_1 is affected by temperature more than k_2, the process should be again performed at the desired maximum temperature to produce R. Either way, the reaction should be stopped at the convenient time where the maximum R amount is recovered. If k_1 is less affected by temperature than k_2, the reaction temperature has to be high at the first part and then it has to be decreased gradually in order to prevent the R loss (Luyben, 1996).

According to the above mentioned information, the relevant mathematical models can be derived assuming constant density. The general equation for the mass which indicates the situation after the reactants has been initially placed and for the beginning of the batch, is given below.

$$\frac{d(\rho V)}{dt} = 0 - 0 \qquad (1.1)$$

Since there is no inflow neither an outflow and the density (ρ) is constant and as a consequence the differential ratio of volume V to time t, the change of volume with time, dV/dt is 0. Therefore the liquid volume is assumed to be constant. The following equations represent the component continuity for A, R and the kinetic relations regarding the relevant reactions in the process. C_A is the concentration of A, C_R is the concentration for R and k is the reaction constant for the relevant process. E_1 and E_2 are the activation energies of the reactions, respectively. $\alpha_1$and α_2 are the preexponential factors for the relevant rate constants. Finally, R_{gas} is the gas constant. Equations through 1.2 – 1.7 are referred from Luyben, 1996.

$$V\frac{(dC_A)}{dt} = -Vk_1C_A \tag{1.2}$$

$$V\frac{(dC_R)}{dt} = Vk_1C_A - Vk_2C_R \tag{1.3}$$

$$k_1 = \propto_1 e^{-E_1/R_{gas}T} \tag{1.4}$$

$$k_2 = \propto_2 e^{-E_2/R_{gas}T} \tag{1.5}$$

A lumped parameter model is used for the reactor metal wall heat content, $H=C_pT$, where C_p is the specific heat capacity and T is the fluid temperature (°C). Consequently, the energy equations of the reaction mixture and for the metal wall are given below.

$$\rho V c_p\frac{dT}{dt} = -\Delta H_{r1}Vk_1C_A - \Delta H_{r2}Vk_2C_R - h_iA_i(T - T_M) \tag{1.6}$$

$$\rho_M V_M c_M\frac{dT_M}{dt} = h_oA_o\left(T_J - T_M\right) - h_iA_i(T_M - T) \tag{1.7}$$

Eq. 1.6 is the energy balance for the reaction mixture and the Eq. 1.7 is energy balance for the metal wall, where ΔH_{r1} and ΔH_{r2} are exothermic heats of reaction. The reaction heating results in conditions where the jacket temperature T_J is higher than the metal wall temperature T_M and T_M is higher than T. The inside film coefficient h_i and the inside wall area A_i affect the heat transmission. Consequently, the density of the metal wall ρ_M, volume of the metal wall V_M, specific heat capacity of metal wall C_M are included in the energy balance for the metal wall, where the energy transmission is affected by the outside film coefficient h_o and the outside area A_o (Luyben, 1996).

1.2. Semi-Batch Processes in Chemical Engineering

Semi batch, semi flow or semi continuous processes take place in single stirred tank with equipments very similar to the ones that are used in batch processes. Most of the time, some of the reactants are fed into the tank primarily and the rest is fed gradually. This type of reactant feed has an advantage where there are large heat effects in the reaction and when high reactant concentrations lead to undesirable intermediate products or when some of the reactants are in gas phase which has a limited solubility. Reactor design of semi batch processes is really the cumbersome part, since it is an open system that operates under nonsteady-state conditions. According to this difficulty, the mass and energy equations for a semi batch process are more complicated than batch or continuous processes (Hill, 1977).

Semi batch behavior is realized when the operating conditions change from one state to another or when operation is shutdown. The most important property of a semi batch process is that some of the reactants are added in the first place and the others are fed continuously, this gives an advantage to control the energy evolution by manipulating the feed rate of the reactant that is fed continuously. Eventually, this control of feed rate affects the reaction rate which is not possible in batch or continuous reactors. Other possibility is to add all the reactants into the reactor and remove at least one of the products continuously, for example as in esterification process where the water is removed by boiling. This removal of product leads to increase the rate and prevention of the reverse reaction.

The variables of semi-batch processes can be given by considering a vessel where C_{Ro} is the initial concentration of R, V_0 is the initial volume, C_{Ao} is the concentration of the feed solution for t and at a volumetric rate v_o. Accordingly, the volume of the solution in the tank, the stoichiometric balance and material balances are given in Equations 1.8 - 1.10 (Perry et al, 1999).

$$V = V_0 + v_o t \tag{1.8}$$

$$v_o t \cdot C_{A_o} - V \cdot C_A = V_0 \cdot C_{R_o} - V \cdot C_R \tag{1.9}$$

$$C_R = C_A + \frac{V_0 C_{R_O} - vtC_{A_O}}{V_0 + v_o t} \tag{1.10}$$

The material balance of A can be defined as the balance of input to the sum of output, sink and accumulation. Since there is no output, the value will be zero. The sink and accumulation terms are defined below.

$$v \cdot C_{A_o} = 0 + kVC_AC_R + \frac{d(VC_A)}{dt} \tag{1.11}$$

By taking the derivatives of concentration and total volume, the equation can be expressed as follows:

$$v \cdot C_{A_o} = kVC_AC_R + V\,\frac{d(C_A)}{dt} + vC_A \tag{1.12}$$

In order to obtain the differential expression of the system, the final equation is rearranged.

$$\frac{d(C_A)}{dt} + kC_AC_R + \frac{vC_A}{V} = \frac{vC_{A_o}}{V} \tag{1.13}$$

By combining these equations, the last balance equation is obtained.

$$\frac{d(C_A)}{dt} = \frac{v}{V_0+vt}\left(C_{A_o} - C_A\right) - kC_A\left(C_A + \frac{V_0C_{R_o} - vtC_{A_o}}{V_0+vt}\right) \tag{1.14}$$

Even if the process is isothermal, such equation should be solved with numerical methods as the above equation is nonlinear.

1.3. Dynamic Behavior of Batch and Semi Batch Processes

In batch process operations, there are three main steps. In the first step which is the amplification of production procedure step, chemist explores the possible synthesis paths in the laboratory. By the explored path for the production, convenient recipes are chosen for the maintenance of concentrations, temperatures or flow rates for the relevant operations to be performed and for a feasible batch operation. Secondarily, in the production planning, resource allocation and scheduling step, the operation should be made beneficial in the existing plant. This should be done with the correct allocation of unit processes to a set of variable devices, followed by the organizing of the subprocesses of an operation to obtain the number of products to be sold. Finally, the reliable and effective step of the production includes the establishment of the performance of units. In this step, the process variables are adjusted within the ranges for the step in question where the recipes are provided. Optimization is important for the safety and operational constraints. Batch processes are nonsteady, so the process variables are time dependent. Therefore in this step time dependent profiles one of the determination techniques is dynamic optimization (Bonvin et al, 2003).

Process optimization reduces production costs, corresponds to safety requirements and environmental regulations, improves the quality of the product, reduces product variability and makes the scale up easier. In the industry, the main objective is the profitability or the payback of the investment. Even if the optimization of the industrial scale processes is important for the gain and profit of a production, mathematical modeling and optimization techniques are not used widely in operations. In industry, the main problem is that the mathematical modeling and optimization techniques are not conducted by reliable models and measurements and also have been lack of the accountability of the optimal solutions and scheme. Generally, batch processes are carried out with less instrumentation in order to compensate model uncertainty, but this has not been available continuously. However, there are some studies to overcome this problem recently. Besides the reliable models and measurements problem, there could be two additional reasons. The interpretability of the optimal solution and the optimization framework also affect the applicability of the techniques to the industrial scale. In order to perform an optimization, a model of the process is used with the optimization path which is called the black box in optimization jargon. The result of these optimizations cannot be used by industry, if the results cannot be integrated easily to industry physically. In literature, the few studies exist with limited numbers with the usage of measurements. In industry since the unpredictability is prevalent, manufacturers and engineers are willing to use such measurements (Bonvin et al, 2003).

1.4. Basics of Optimization for Batch and Semi Batch Processes

The most suitable adaptations in a batch process or the best optimization choices are numerous. One of which is to combine few operations in a single equipment as in heating the feed and allowing the reaction to occur in the same vessel, while ensuring that these do not limit the cycle time. Another choice is to overlap batches by providing more than one batch at different processing stages at any given time. In order to limit the batch cycle time, the two options of introducing parallel operation to steps and introducing multiple operations in series into steps are possible. Adjustments in equipment size can also give some options in optimization. When the size of the equipment of a step that limits the batch cycle time is increased, the dead time for the steps that are not limiting can be reduced. On the other hand, decreasing the size of the equipment of a nonlimiting step increases the time for these steps and results in reduction of the dead time for nonlimiting steps. Finally another optimization choice can be considered as storing the intermediate between batches. The variables in a batch process are batch size, cycle time, number of batch units both in parallel or series, size of the equipment and intermediate storage. Besides these variables, there are still other variables like reactor conversion and recycle inert concentration, even if they are considered in continuous processes, they are results of a batch process nature (Smith, 2005).

Optimization is the decision of choosing the best alternative for an action. The calculus is used in the actual computational procedure or in the proof of the validity of the method. The theorems of linear vector spaces or theory of inequalities are used. The problems that occur in calculus which are a linear programming technique are linear objective function and linear constraints. For inequality theory, problems like nonlinear objective, no constraints, nonlinear constraints, polynomial objective and polynomial constraints are faced. In an optimization problem, the variables are classified as independent, input and state or output variables. For example in a batch reactor, input variables can be initial batch composition, initial temperature, the rate of agitation and the extent of external heat transfer. The output variables in a batch reactor can be instantaneous composition, instantaneous temperature and possibly instantaneous pressure (Ray and Szekely, 1973).

The most important step in optimization is problem formulation, which identifies the fundamental elements of theoretical or verbal statements of the given process. Problem formulation rearranges the essential elements in a mathematical form as the objective function and the process model, where the objective function can be named as economic criterion and process model as constraints. Key variables of the process can be represented by profit, cost, energy and yield in the objective function. The relationship between the key variables is called process model. A mathematical model is constructed for a system which exists or which will be generated, where this model represents the essential aspects which present knowledge of that system in a usable form. Optimization applications consist of the mathematical expressions which are models that are based on physical and chemical laws. Chemical laws refer to mass/energy balances, thermodynamics and chemical reaction kinetics. Empirical models are used in spite of the unavailability of a physical model where the time and the resources are constrained (Himmelblau and Edgar, 2001).

In order to build a model for the optimization of such a system, the following steps should be considered as the pathway. First step is the problem definition and formulation. In this step, number of independent variables, number of independent equations and number of unknown parameters are defined. Second step is the preliminary and detailed analysis where the design phase includes specification of the information content, general description of programming logic and algorithms. These items are used to improve and engage a useful model, formulation of the mathematical description of such a model, and simulation of the model. Third step is the evaluation and the model is checked finally as a whole. Finally the fourth step includes the interpretation application (Himmelblau and Edgar, 2001).

Typical industrial companies use optimization in three main areas, such as management, process design and equipment specification and plant operations. The management optimization means evaluating the projects, selecting products, defining the corporate budget, decision of investing in sales regarding with the research and development and new plant construction benefits. Process design and equipment means the choice of process and the conditions of operation. Finally, plant operations are the control of operations for a given unit at determined temperatures, pressures or flow rates that are best in some sense. Plant operations also deal with appropriation of raw materials on periodical basis and overall picture of shipping, transportation, distribution of products to lead to minimal costs. Besides management, process and equipment and plant operation areas, there are other important attributes to be optimized. These are sales limited by production and market, large unit throughputs, high raw material or energy consumption, product quality which exceeds product specifications, losses of valuable components through waste streams and high labor costs. Therefore, the valuable data for identifying opportunities are profit and loss statements for the plant or the unit, periodic operating records for the plant. Engineers, managers or related people do the optimization for projects. First of all they determine best sites for plant location. They route tankers for the distribution of products. Engineers size and prepare a layout of a pipeline, design equipment and an entire plant, schedule maintenance and equipment replacement. The operating equipment choice is also performed by engineers. Finally engineers/managers evaluate data to construct a model of a process, to minimize inventory expenses, to allocate resources or services among several processes, to plan and schedule construction. In these projects or problems to be solved, the essential features are at least one objective function, equality constraints and inequality constraints (Himmelblau and Edgar, 2001).

In batch process operations, since there are no steady state conditions, the process variables go through significant changes during the batch process time. Therefore, the major objective in batch operations is to find an objective function to express the system performance. The examples of optimization of an objective function include the achievement of a product yield with a profitable economy or maximization of the product quality/yield for the given batch time. In the presence of the constraints, optimization is performed and additionally state dependent constraints can be limited, which are precepted by limitations. Temperature and concentration limits are categorized under safety and operability deliberations and as a result of these, state-dependent constraints arise. As a result of selectivity or performance deliberations, the terminal constraints arise. In a batch reactor where multiple reactions occur, it is preferred to maintain a below-limit concentration of some species to accelerate the process or cancel further downstream processing. Therefore, batch optimization problems which fall under the category of dynamic optimization problems, deal with dynamic and static constraints (Bonvin et al, 2003).

Further information about optimization, how to implement models and how to develop models in real time scale will be discussed in Chapter 3.

Chapter 2

2. Dynamic Mathematical Models of Batch and Semi Batch Processes

In this section, mathematical models and their relation to batch and semi batch processes will be discussed by giving the principles and classification of models as empirical and physical models.

2.1. What is a Dynamic Mathematical Model?

A mathematical model is expressing the essential features of a physical system in mathematical terms. In a general statement, it can be represented as follows:

$$\left(\begin{matrix}dependent\\ variables\end{matrix}\right) = f\left(\begin{matrix}independent\\ variables\end{matrix}, parameters, forcing\ functions\right) \tag{2.1}$$

Dependent variable is a property that usually represents the behavior/state of a system. Independent variables are values like time and space, where the determination of the system behavior is performed. Parameters give the properties or species of a system and the forcing functions express the external effects acting upon the system (Chapra and Canale, 2008).

Dynamic models are used for improving the understanding of the process, training plant operating personnel, developing a control strategy for a new process and optimizing process operating conditions. Dynamic models and also the computer simulation allow the investigation of transient behavior without any disturbance of the process. Furthermore, simulation gives the chance of getting valuable information about dynamic and steady-state behaviors even before plant is constructed. After the plant is constructed, operators are responsible for running the complex units in the process, thus their training is essential and crucial. Process simulators help to train the operators and also they allow easy communication with operators. The interface of process simulator to standard process control equipment, a realistic environment is created for the operators and it can help dealing with emergency situations in real time. Alternative control strategies can be generated for a dynamic model of a process in order to be assessed in different aspects (Edgar, 2003).

Optimization problems concern about three main models. Theoretical models, empirical models and semi-empirical models are the methods used for modeling in optimization. Theoretical models use principles of chemistry, physics and biology. They have advantages of providing physical judgment into process behavior and application over expanded ranges of conditions. However there are some disadvantages of theoretical models, such as being costly, time consuming and depending on the complexity of the processes. Empirical models are about fitting experimental data into already known equations. These kinds of models are easy to develop but they cannot be extrapolated well and the range of data is limited. Semi-empirical models are the combination of two models as it can be figured out from its name. Combining these two models results in cancelling each other's disadvantages and consequently resulting in incorporate theoretical knowledge, can be extrapolated over a wider range of operating conditions, require less development effort (Edgar, 2003).

In optimization of chemical processes, the development of dynamic models includes ordinary differential equations, partial differential equations and algebraic equations. Algebraic equations like vapor-liquid equilibrium, heat transfer correlation, reaction rate expressions are included in process models which are from vapor-liquid equilibrium, heat transfer correlation, and reaction rate expressions. Simply, the path can be defined by the following steps. First of all, the modeling objectives and the end use of the model should be stated. The required levels of model details and accuracy are determined. The schematic diagram of the process and all variables is drawn in order to visualize the problem. All assumptions related to the model should be listed. The importance of the spatial variations of process variables should be determined and then the balance equations must be written. In case of any need, the other algebraic equations must be involved and defined. Degrees of freedom analysis should be performed followed by the simplification of the model. Finally, the inputs are classified as disturbance or manipulated variables (Edgar, 2003).

2.1.1. Physical Models and Empirical Models in Optimization

In developing a dynamic process model, either a first principle based physical models are used or empirical models are used. The physical models are conducted by the combination of conservation laws which are the mass, energy, and momentum conservation balance equations. The resulting physical models typically have sets of differential and algebraic equations and they must be solved concurrently. Empirical models, involve hypothesizing the form of a dynamic model, which is called the transfer function and such transfer function includes a number of parameters that need to be predicted. For the development of these models, the most expensive step is the verification of the accuracy for the prediction of plant behavior (Perry et al, 1999).

2.1.2. Principles of Formulation

Principles of formulation in optimization problems were explained in a detailed way by Luyben. Therefore the basis, assumptions, mathematical consistency of model, solution of the model equations and finally the verification for the optimization problems will be discussed consecutively (Luyben, 1996).

Basis for Mathematical Models

Mathematical models are made up of physical and chemical laws. Mass, energy and momentum conservation laws are used. Therefore, throughout the solution of the dynamic optimization problem, these laws will be used within the relevant equations.

Assumptions in Mathematical Models

An engineer has to exercise his engineering judgment by deciding about the valid assumptions in modeling. An engineer always works for an answer which includes a precise description and an adequate level which can be called “optimum sloppiness”. This term involves the prediction of estimations to simplify as possible without being oblivious. In practice, this optimum condition refers to a complexity as the available gauging facilities will permit.

Mathematical Consistency of Models

After obtaining all the equations for the mathematical model, the number of variables should be equal to the number of equations in order to sustain a systematic optimization approach. When the “degrees of freedom” is zero for a system, a solution can be obtained. On the other hand, the system is underspecified or over specified which leads to a dead end for the solution. All terms should be checked in order to be consistent regarding their units, where this is an important and essential step in mathematical consistency of models. In most of the problems in life, time dependency is important, therefore when the one is dealing with dynamic models, time dependency becomes the subject to be careful about, since dynamic models are representation of systems that change according to time (Luyben, 1996).

Solution of the Model Equations

The solution of the model equations are finally done by the computer programming. The most suitable algorithms and the most relevant models are chosen for the problem. Then the computer program is used with a simultaneous process control devices in order to link the outcomes of the relevant process to the computer programming for tracking the changes and simulating the process (Luyben, 1996). Solution of the model equations will be explained in Section 3.

Verification

When conducting a mathematical model, most of the time it is difficult to express the real world situation exactly where sometimes the plant is not build yet. The model has to provide a proof of a real world situation. However, some supportive data can be obtained from the similar plants or a pilot plant of the future industrial scale plant. As a result, the verification step is the most important step, since the developed model is to be used in a large scale plant and though, the validity testing of the model can be a real challenge (Luyben, 1996).

2.2. Why Do We Need Dynamic Mathematical Models?

A developed mathematical model in a chemical engineering system concludes that the most important part is to understand the key element which makes the process to be realized. In order to understand the basis of a system, the confusion factors should be eliminated and this can be achieved by observation. By observation, the relationship between the variables can be seen more clearly. Mathematical models can be convenient in all areas and stages of chemical engineering aspects.

1. ***Research and development:*** In research and development stage, the mechanisms and parameters are determined according to laboratory or pilot scale data. Also different operational condition effects are explored which help in calculations.
2. ***Design:*** In order to have dynamic performance, size and arrangement of equipment should be determined. The interaction of different process stages should be studied as well as the evaluation of alternative process and control structures and strategies should be carried out and simulating start-up, shutdown,

and emergency situations and procedures must be planned.

3. ***Plant operation:*** Checking and processing the problems, helping in start-up of operations and provide the training of employees that are relevant to production, observing and concluding the requirements for further projects, optimization of plant operation is the steps for plant operation (Luyben, 1996).

Dynamic mathematical models are used in the solution of dynamic optimization problems and batch optimization problems fall under this category. In batch optimization problems, there are both static and dynamic constraints. For the classification, the uncertainties should be defined. Uncertainties can be either variations in initial conditions or uncertain model parameters or process disturbances. Naturally, it is likely to cancel the ambiguity and provide the solution of optimization problem with a nominal solution. However, in batch processes since the conditions are unstable and dynamic, it may not be feasible in the presence of uncertainty. The second step of classification is about the information type. This information is used for dealing with the uncertainty. After the description of the problem, constraints, objective function and other characteristics of the optimization problem, the simulation of dynamic model stage comes. Linear dynamic models are particularly useful for analyzing control-system behavior (Bonvin et al, 2003; Bonvin et al, 2002).

In the next chapter, model based optimization of batch and semi batch processes will be discussed along with the techniques to be used in order to optimize such processes.

Chapter 3

In this chapter, dynamic optimization and control vector iteration which is the solution technique, will be explained by examples.

3. Model Based Optimization of Batch and Semi Batch Processes

First of all, it would be necessary to explain the close relation between model based optimization, dynamic optimization and optimal control. Dynamic optimization is the process of minimizing or maximizing the costs/benefits of some objective function over a period of time. Dynamic optimization may be called as optimal control sometimes. Therefore it will be clarifying to explain the term and concept of optimal control. Optimal control is the modern approach to the dynamic optimization. In optimal control, there are no constraint variables and therefore this solution approach relies on differentiability. Control variables are used to optimize the optimization variables to reach a certain objective. When the optimal path or the control variable values are found, the solution to the state variables or the optimal paths for the state variables is derived.

Dynamic optimization of batch and semi batch systems can be provided by the dynamic models and/or empirical models developed for these systems. The principles of both optimal control and dynamic optimization concepts in solving the model equations and objective functions are similar. However, differing from the optimal control, control variables are determined as feed-forward in order to perform the dynamic optimization. Batch, semi-batch processes, start up and shut-down of continuous processes are unsteady state and thus show dynamic changes during the operation. The objective function such as the minimum time, maximum conversion, minimum energy or minimum cost should be implemented in the algorithm of piecewise dynamic optimization. In addition, the piecewise optimization constraints with the upper and lower boundaries should also be defined in compliance with the model and variables.

The following optimization problems include practicable solutions for semi-batch and batch processes. For semi-batch processes like coal burning stove where the reaction is carried out as semi-batch because of the CO, heat and CO_2 output or a CaO hydration reactor for thermo-chemical heat pump process (Fig. 3.1), the applicable solution pathways will be explained in detail in the following subsections. For batch processes encountered in pharmaceutical and food industry, there are no inputs or outputs during the process. Therefore, the possible solutions will be presented in sections 3.1, 3.2 and 3.3.

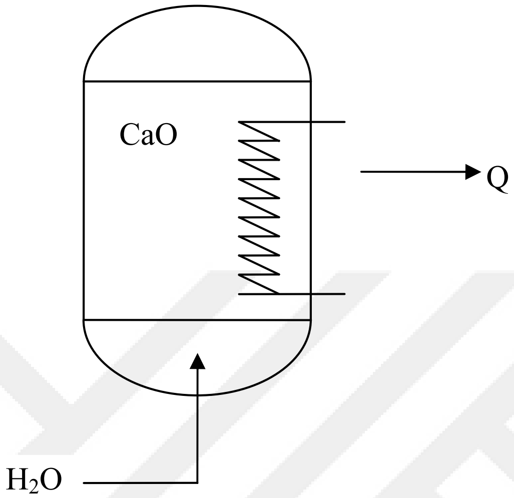


Figure 3.1 Semi-batch Calcium hydroxide manufacturing reactor (example of chemical heat storage).

$$CaO_{(s)} + H_2O_{(v)} \leftrightarrow Ca(OH)_2 + \Delta H \tag{3.1}$$

Calcium hydroxide, with the chemical formula $Ca(OH)_2$ is an odorless, colorless crystal or white powder and is attained when calcium oxide is quenched with water. It conducts a high pH in a water (>12 in a saturated solution). It is stable under ordinary conditions and storage. Calcium hydroxide is refined from limestone. The first step is to heat limestone in order to form calcium oxide. The second step is the reaction of the calcium oxide with water to form calcium hydroxide and heat. By this hydration reaction, the calcium oxide breaks down into fine particles of calcium hydroxide.

The hydration reaction (Eq. 3.1.) takes place with a negative Gibbs free energy. Since spontaneous reactions occur with a negative Gibbs free energy and the Gibbs free energy is the difference between heat and entropy at a given temperature (Eq. 3.2.), Equation 3.6. is obtained. For this kind of specific reaction, assuming that the equilibrium temperature is approximately 600°C, there can be two reactions to occur according to the equilibrium temperature, $T_{eq} \cong 600°C$.

$$\Delta G = \Delta H - T\Delta S \tag{3.2}$$

$$\Delta G \leq 0 \tag{3.3}$$

$$\Delta H - T\Delta S \leq 0 \tag{3.4}$$

$$\Delta H \leq T\Delta S \tag{3.5}$$

$$\frac{\Delta H}{\Delta S}\left(\frac{J/mol}{J/molK}\right) \leq T[\equiv]K \tag{3.6}$$

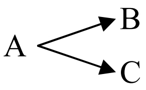
$$CaO_{(s)} + H_2O_{(v)} \overset{1}{\rightarrow} Ca(OH)_2 + \Delta H \qquad T < 600°C \tag{3.7}$$

$$Ca(OH)_2 + \Delta H \overset{2}{\rightarrow} CaO_{(s)} + H_2O_{(v)} \qquad T > 600°C \tag{3.8}$$

In such a reaction, important control variables are water vapor feed rate, heat removal rate due to the exothermicity of the reaction. Furthermore, the adjustment of the water vapor feed rate is crucial as it controls the reaction rate and thus the heat release rate. Hydration reaction ceases in this kind of reaction when there is no water vapor (Eq. 3.7). Since the equilibrium temperature is 600°C, at temperatures above this value or in other words if the heat produced by the hydration reaction (Eq. 3.8) is not removed, the reversible reaction which is the dehydration reaction takes place and it causes the heat storage to work inefficiently.

3.1. Dynamic Optimization of a Parallel Reaction

Considering an example where an adiabatic batch reactor operates under 1 hour period and produces two products according to a parallel reaction mechanism where B and C are produced in a parallel way by the reaction of A. As an example for the operating system, both of the reactions are irreversible and reactions are in first order where $k = \alpha\exp\{-E/R_{gas}T\}$. If the aim of the problem is to find the temperature and time profile that maximizes the output of B for operating temperatures below 139°C, the objective function, variables, equality constraints and inequality constraints should be defined (Himmelblau and Edgar, 2001).



In the problem described above , the objective function is to maximize the yield of B, pretending that C is an undesired product in the environment and therefore the reaction should be favored mostly to give B. The following equations are used for defining the reaction rates and also mass balances referred from Himmelblau and Edgar, 2001.

$$\frac{dA}{dt} = -(k_1 + k_2)A \tag{3.9}$$

$$\frac{dB}{dt} = k_1 A \tag{3.10}$$

In order to build up the solution path for the relevant problem, the initial conditions are also equality constraints together with the fixed period of time (1-hour) and the maximum temperature allowed is the inequality constraint.

$A(0) = A_0$

$B(0) = 0$

$\mathrm{T} \leq 139°\mathrm{C}$

$\mathrm{t_{max}} \leq 1$ hour

For the solution path of the relevant optimization problem, the independent variable is temperature profile as a function of time, because the time is fixed as 1-h period of reaction. The dependent variables are concentrations of A and B.

Finally, the inequality constraints of the relevant optimization problem are the restricting condition of temperature being below 139°C but above zero and concentrations of A, B and t are being positive values. In order to solve this kind of problem, the analytical solution to find the concentrations of A and B vs temperature should be considered for minimization (Fig. 3.2. and 3.3.). ODEs should be converted into difference equations and minimization should be done using an iterative solution procedure. The collocation of constraints should be carried out as an approximate solution to minimize and finally some transformations should be performed to simplify the solution.

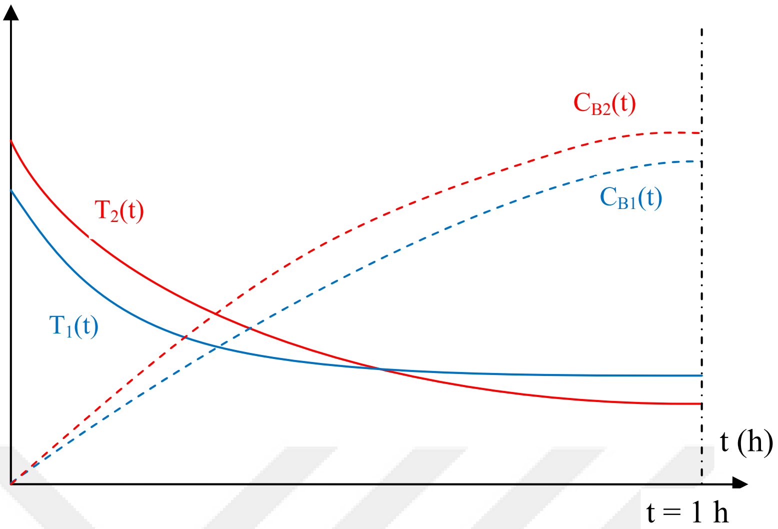


Figure 3.2 Visual representation of concentration change of B due to different temperature profiles.

Considering the parallel reaction of A, B and C, since B is the desired product, the concentration profile of B due to different temperature profiles are shown in Fig. 3.2. If the temperature profile for the reaction is $T_1(t)$, the concentration profile for the desired product B can be represented as $C_{B1}(t)$. The temperature for the reaction also can be $T_2(t)$ and the concentration profile can be $C_{B2}(t)$. There can be various alternative temperature profiles for the reaction and as a result of the relevant temperature profiles, there can be various concentration profiles. However the objective is to find the maximum yield of desired product B. For this objective, different temperature profiles should be experimented and investigated to find the maximum optimal yield of B.

In this parallel reaction, when B is produced, also C is going to be produced. However, due to the choice of temperature profiles, the yield of B and the yield of C will be affected. If the temperature profile for the reaction is $T_1(t)$, the concentration of B will show a higher yield according to C. However if the temperature profile of the reaction is $T_2(t)$, maybe the concentration profile of B will be as it is shown in the figure and it causes the yield of C to be higher. The higher yield or a higher concentration of C is not a desired situation. Since the desired product is B, the temperature profile should be chosen at such a path where the yield or the concentration of C does not overshoot the yield of B or affect the yield of B negatively.

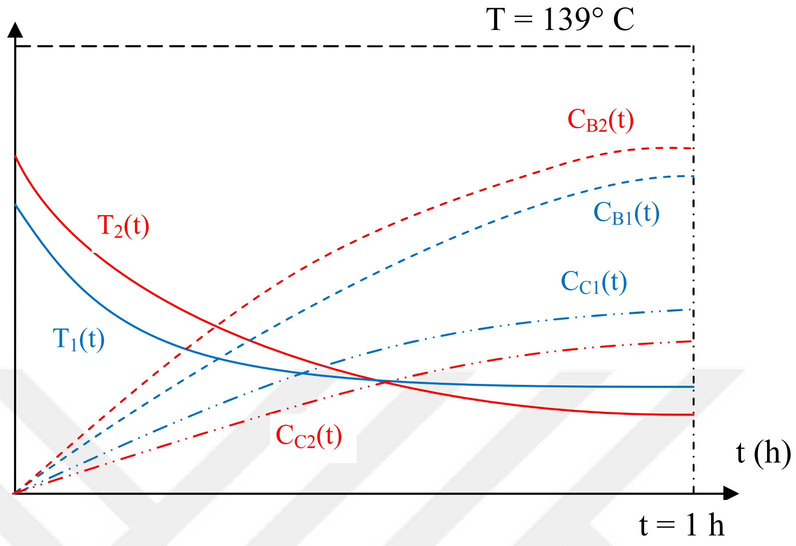


Figure 3.3 Visual representation of concentration changes of B and C due to different temperature profiles.

Furthermore, these assumptions and experiments should take place within the limits of equality constraints which are $T \leq 139°C$ and $t = 1$ h. Depending on the process and subprocesses, these constraints can be more in number and difficult to fit in every condition for the problem in question.

3.2. Dynamic Optimization of a Multiple Stage Reactor

Considering a series of four reactors that are operating under isothermal and well-mixed conditions, the following figure can be drawn. The tanks have a total volume of V_i=20 m^3, without having the same volume with each other. In each tank the reaction takes place with a mechanism $r = -kC^n$. In order to find the tank volumes for steady-state operation with a fixed fluid flow, the residence time should be taken as $(V_i/q_i)=\theta_i$. The following data for the relevant solution are n (the degree of the reaction), k, C_0 (initial concentration value) and q (fluid flow rate). The objective function of the relevant problem is to maximize C_4. Since the system is consecutive, all the reaction parameters as the inputs will be used in the following series reactors set up.

Therefore, the final output which is the concentration of the final tank C_4 should be maximized (Himmelblau and Edgar, 2001).

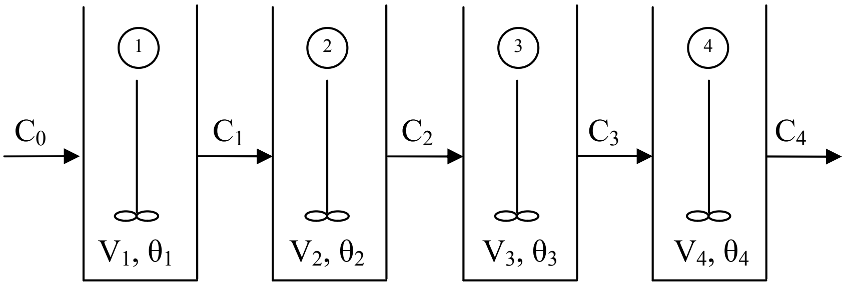


Figure 3.4 Four series reactors (adapted from Himmelblau and Edgar, 2001).

In every optimization problem, the objective function, the variables, the equality and inequality constraints should be defined in order to solve the problem. In this example, the dependent variables are C_1, C_2, C_3 and C_4. Because these are the outputs of the relevant reactions where they depend on θ_i, q_i and V_i. Therefore, θ_i is the independent variable for each of the reactors. Naturally, every optimization problem includes constraints. The equality constraints for this example are the ratio of total volume to the fluid flow rate and the material balances which are expressed as follows:

$$C_0 = C_1 + \theta_1 k C_1^n \tag{3.11}$$

$$C_1 = C_2 + \theta_2 k C_2^n \tag{3.12}$$

$$C_2 = C_3 + \theta_3 k C_3^n \tag{3.13}$$

$$C_3 = C_4 + \theta_4 k C_4^n \tag{3.14}$$

Finally, the inequality constraints of the problem are $\theta_i \geq 0$ and $C_i \geq 0$, because these values cannot be negative in such a problem.

3.3. Dynamic Optimization of a Series Reaction

3.3.1. Isothermal Reaction

Considering a consecutive unimolecular-type first order isothermal reaction, in order to find the time when the desired product R is at its maximum yield, all of the rate equations should be included in the solution of the problem.

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

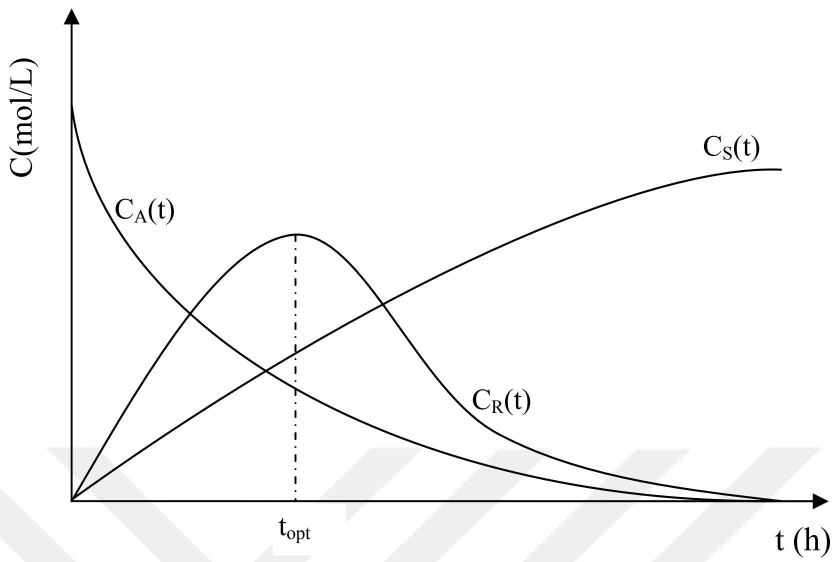


Figure 3.5 Visual representation of concentration change of A, R and S.

In Figure 3.5., concentration of component A continuously decreases because of the conversion to R and S consecutively. The concentration of product S of the side reaction, continuously increases. However the desired product R's concentration first increases due to the first reaction which is A → R with the reaction rate constant k_1. There is a second series reaction where R is converted into S. After reaching the maximum concentration of R both concentrations of R and A decrease while S increases. As a result, the objective function for this problem is to maximize the concentration of R where the time is expressed as optimal time, t_{opt}, on the above given figure. Optimal time means that the conversion of A is at such a point where R is at its maximum during the whole progress of the series reaction. Besides defining the objective function, independent, dependent variables and equality, inequality constraints should be defined. In this kind of optimization problem, the independent variable is time, t. The concentration of A, R and S are the dependent variables. The concentrations of A, R and S vary with time. The equality constraints which are also the model equations can be defined as follows.

$$\frac{dC_A}{dt} = -k_1 C_A \tag{3.15}$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R \tag{3.16}$$

In these equality constraints, C_A and C_R are the concentrations of A and R consecutively. k_1 and k_2 are the reaction rate constants and do not depend on the temperature, since the reaction is isothermal.

The inequality constraints are C_A, C_R, C_S, t being above zero.

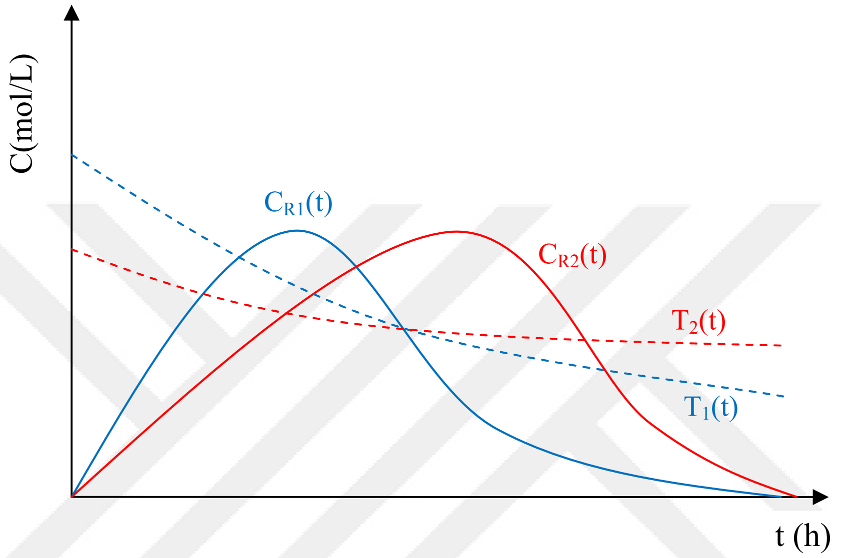


Figure 3.6 Visual representation of concentration change of R due to different temperature profiles.

In Figure 3.6., two different concentration profiles with time are shown according to two different temperature profiles. These assumptions show that, if the temperature profile of a reaction is T_2, the maximum concentration of R will be seen at a later time period, for example, at t = 2 h. On the contrary, if the temperature profile is T_1, the maximum concentration of R will be obtained at an earlier time period, e.g. at t = 45 min. The local/absolute maximum of the concentration can be found by reliable optimization.

In every reaction of a process, there is an absolute maximum/minimum and/or local maximum/minimum. As a mathematical expression, the absolute maximum of a function on a domain is if and only if $f(x) \leq f(c)$ for all x in domain, where f(c) is the output value. The absolute minimum of a function on a domain is if and only if $f(x) \geq$

f(c) for all x in domain, where f(c) is again the output value. On the other hand, the local maximum of a point is if and only if f(x) ≤ f(c) for all x in some open interval containing c. The local minimum of a point is if and only if f(x) ≥ f(c) for all x in some open interval containing c, where c is an interior point of the domain of the function f. Sometimes absolute maximum or minimum can be called global maximum or minimum, as well as local maximum or minimum can be called relative maximum or minimum. Fig. 3.7 shows the absolute/global extrema and local/relative extrema.

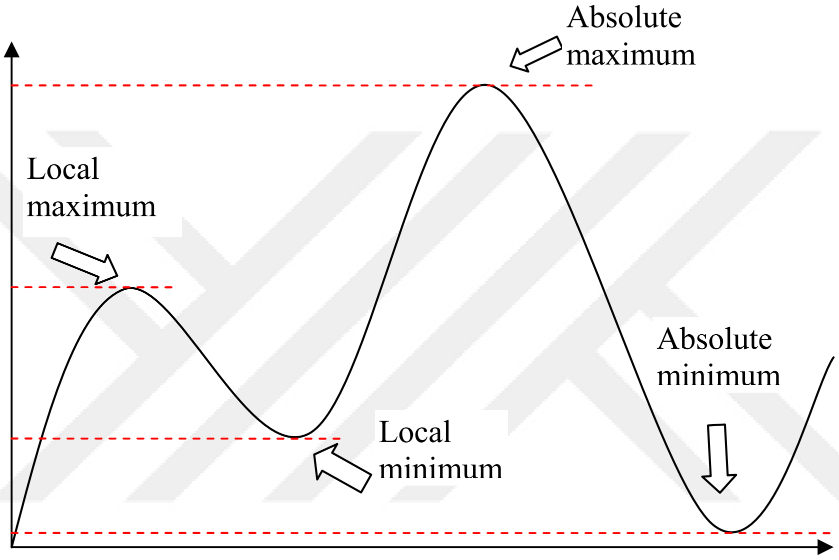


Figure 3.7 Visual representation of absolute and local extrema.

As a solution procedure, there is a possible solution with a first order linear differential equation integrating factor.

$$\frac{dC_A}{dt} = -k_1 C_A \tag{3.15}$$

By the integration of the reaction rate equation, concentration of A is obtained in terms of reaction rate constant, time and initial concentration of A.

$$C_A = C_{A_0} e^{-k_1 t} \tag{3.17}$$

By substituting C_A into the rate equation of R, a complex differential equation is obtained.

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R \tag{3.16}$$

$$\frac{dC_R}{dt} = k_1 C_{A_0} e^{-k_1 t} - k_2 C_R \tag{3.18}$$

This kind of differential equation can be solved by multiplying by the first order linear differential equation integrating factor as it was mentioned before.

$$\mu(t) = e^{\int k_2 dt} = e^{k_2 t} \tag{3.19}$$

The detailed solution and related examples for different reaction orders (first reaction is zero order, second reaction is first order and first reaction is first order, second reaction is zero order), non isothermal reaction, are given in Appendix A.

3.3.2. Non-isothermal Reaction

Considering a consecutive unimolecular-type first order non-isothermal reaction, in order to find the time when the desired product R is at its maximum yield, all of the rate equations should be included in the solution of the problem (Jensen and Jeffreys, 1977).

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

When the reaction is non-isothermal, differing from the isothermal reaction, the reaction rate constants depend on temperature which needs to be optimized. In this case, Arrhenius equation will be used. Recalling from the equations 1.4 and 1.5, reaction rate constants can be expressed as follows:

$$k_1 = \propto_1 e^{-E_1/R_{gas}T} \tag{3.20}$$

$$k_2 = \propto_2 e^{-E_2/R_{gas}T} \tag{3.21}$$

Therefore, the material and energy balances should be defined according to these rate constants. Additionally, differential dynamic energy balance and spiral heater or jacket energy balance should be written. By substituting the Arrhenius equations into the rate equations, equations 3.25 and 3.26 are obtained.

$$r_A = \frac{dC_A}{dt} = -\propto_1 e^{-E_1/R_{gas}T} C_A \tag{3.22}$$

$$r_R = \frac{dC_R}{dt} = \propto_1 e^{-E_1/R_{gas}T} C_A - \propto_2 e^{-E_2/R_{gas}T} C_R \tag{3.23}$$

For a reactor with a jacket heater, the below mentioned energy balance equation can be stated.

$$V \cdot \rho \cdot C_p \cdot \frac{dT}{dt} = -r_A \cdot \Delta H_1 - r_R \cdot \Delta H_2 - U \cdot A \cdot \left(T_j - T\right) \tag{3.24}$$

In the above mentioned equation dT(t)/dt is the expression for the temperature change in the reactor according to time. Since the reaction rates (r_A and r_R) depend on time, the relevant substitutions should be done and finally equation 3.28 is obtained.

$$V \cdot \rho \cdot C_p \cdot \frac{dT}{dt} = -\propto_1 e^{-E_1/R_{gas}T} C_A \cdot \Delta H_1 - \propto_1 e^{-E_1/R_{gas}T} C_A - \propto_2 e^{-E_2/R_{gas}T} C_R \cdot \Delta H_2 - U \cdot A \cdot \left(T_j - T\right) \tag{3.25}$$

From the equation above, it can be seen that all of the expressions are in terms of T(t) or in terms of t. Therefore, speaking theoretically, this equation contains time dependent variables. Nevertheless, the expression $e^{-E_1/R_{gas}T(t)}$ is a nonlinear coefficient for T(t). However, this problem cannot be solved by analytical solutions, because of the nonlinearity in Eq. 3.25. Consequently, these kinds of optimization problems can be solved by two approaches.

i. The approach where the energy balance equations are neglected and only the optimum temperature profile is studied.
ii. The approach where the energy balance equations are considered and therefore heater temperature, even the vapor flow rate used in the heater or electrical energy consumption are subject to optimization.

For the solution, if the first approach is used, without considering any energy balance equation, the value for k_1 can be found. This means that there is only one interval result which leads to find k_1 for different intervals and finalize the temperature profile according to these separate values. If the second approach is used, the solution becomes a complex situation and the iterative solution is inevitable.

As a result, because of the nonlinearity of the dynamic models for non-isothermal systems, these problems cannot be solved by analytical methods but can be solved with iterative numerical methods. Accordingly, the optimization of non-isothermal systems is performed by using iterative methods by the computer.

3.4. Solution Procedure (Control Vector Iteration)

Leaving the states intact and approximate only the control variables as piecewise constants or with some higher order approximations is called control vector iteration (CVI). The main advantage of this method is the iteration of the control trajectory (Hirmajer et al, 2008). Additionally to the methods mentioned in the source, the optimization of batch processes is possible by Simulink and Optimization Toolbox of the software Matlab®.

Another approach for the CVI considering dynamic optimization was studied as a method for the optimization of dynamic systems by direct sequential/single-shooting approach bases by using problem-adapted discretizations. In this approach, the control profiles are parameterized and the optimization problem is converted into a nonlinear programming (Schlegel et al, 2005).

A major defect of control vector optimization is the low optimization efficiency caused by calculating relevant differential equations in the generated nonlinear programming (NLP) repeatedly. This limits its wide application in the engineering optimization for the industrial dynamic processes due to its time consuming iterative approach to adjust the optimal values of the control vector steps (Liu, 2015).

Summarizing the contents of the above mentioned articles, CVI is splitting the problem into piecewise intervals, in order to control the whole process with a piecewise optimization. In the CVI approach, only the control vector variables are discretized explicitly. The discretization parameters are used as the decision variables for optimization. The profiles of state variables are obtained with forward numerical integration of the differential algebraic equation system for a given input. For the discretizations of the control profiles, often piecewise polynomial approximations are applied.

CVI and the easiest and the hardest applicable pathways will be discussed with an example of a brief explanation graph. Fig. 3.8 shows how the intervals can be applied or chosen during the progress of a batch or semi-batch process.

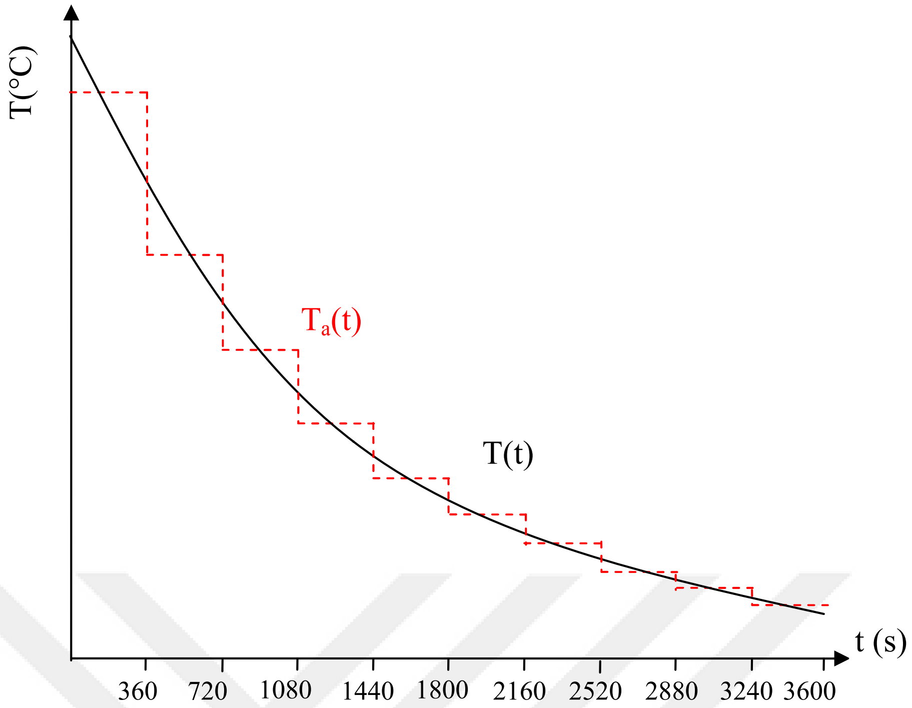


Figure 3.8 Visual representation of control vector iteration application on a temperature profile.

Regarding Fig. 3.8, T(t) is a temperature profile example for a 1-h period process. $T_a(t)$ is an example of CVI time intervals. The intervals can be chosen as listed in Table 3.1. Δt (interval) is 360 s for the example.

Table 3.1. Temperature values corresponding to time intervals.

$T_a(t)$	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
$t_{interval}$ (s)	0 to 360	361 to 720	721 to 1080	1081 to 1440	1441 to 1800	1801 to 2160	2161 to 2520	2521 to 2880	2881 to 3240	3241 to 3600

Besides the solution procedure given in Fig. 3.8, there can be various solution procedures and CVIs. In Fig. 3.9, there are examples for single and multiple scale spaces. As it can be seen from the figures, there can be either a single stage (S_0) or there can be up to many stages (S_2). The time intervals are chosen according to the efficiency and the solution path for the problem. The main objective is to find the suitable temperature profile for the maximum yield of the desired product. The second decision is to find the number of intervals to be chosen for the relevant temperature profile. The easiest way is to choose one step (SS_0). However, this means that the temperature is constant at a constant set point during the reaction progress, which is an isothermal reaction.

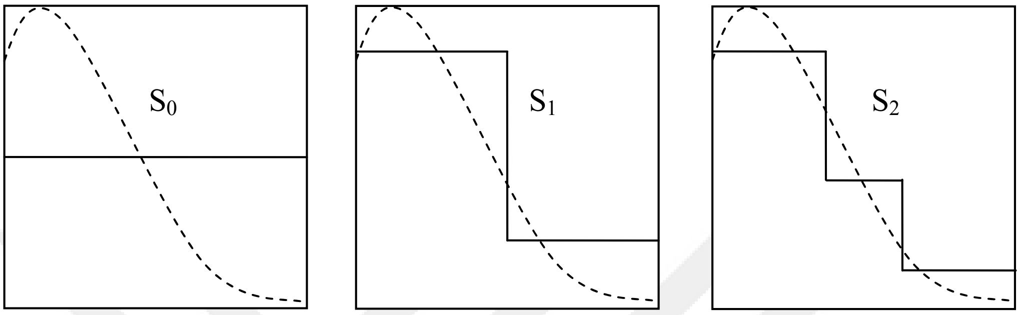


Figure 3.9 Piecewise control vector iteration profiles adapted from Schlegel et al, 2005.

As a result, it is not the best way to optimize a reaction with a single step CVI. The sophisticated way is to find an optimal temperature for each second or each unit time and to design the system according to this approach. Excessive number of steps causes the labor and increases the costs in addition to the complexity of the design and operation of the process. As the labor and the cost increase the operation time will increase and consequently the risk of computation and operation errors will be unavoidable. Besides CVI, there can be other solution alternative which is represented as a quadratic equation (Eq. 3.26) and the best suitable coefficients can be found.

$$T(t) = at^2 + bt + c \tag{3.26}$$

Chapter 4

4. Results and Discussion

Batch and semi-batch processes were explained previously and their dynamic behaviors were discussed. According to the examples on Chapter 3, the results and more complicated examples will be tried to be solved in this chapter by trajectory optimization and control vector iteration techniques. Besides these techniques the solution path will be adapted from Euler's method.

4.1. Optimization for Isothermal Reactors

4.1.1. Batch Reactor

For the following examples, Euler's method (EM) has been used to provide the solution path for the optimization. EM provides an approximation for the solution of an ordinary differential equation. The idea of the EM is to use the concept of local linearity to adhere multiple small line segments so finally an approximation of the actual curve is obtained. The three main elements that are used to build up EM are initial point which is the starting point (initial conditions), step size or increments and the differential equation. EM is used for the solution of complex differential equations by an approximation and here, it will be used for the solution of the isothermal batch series reaction to compare the analytical and numerical methods to solve equations 3.15 and 3.16.

In this section, Tables 4.1 and 4.2, Figures 4.1 – 4.8 are given to show and discuss how healthy is to use the EM for the solution of optimization problems formed of ordinary differential equations. Figures 4.1 – 4.8 are obtained by MATLAB® by solving the given equations in the previous chapters.

From Table 4.1, it can be concluded that the maximum concentration of R has been achieved at Trial 4. Furthermore, it can be seen that as the reaction rate constant for the second reaction gets slower, the difference between the concentration obtained by analytical and numerical methods gets smaller. However when difference between two reaction rate constants is the highest, the maximum concentration of R is achieved.

Table 4.1 Optimal time due to various rate constants (Total time = 100 min).

Trial	**k_1 (1/min)**	**k_2 (1/min)**	**dt (Ana)**	**dt (Num)**	**t_{opt} (min)**	**C_{Rmax} (Ana)**	**C_{Rmax} (Num)**
1	0.1	0.05	1.0	1.0	13.86	5.00	5.18
2	0.1	0.01	1.0	1.0	25.58	7.74	7.84
3	0.1	0.005	1.0	1.0	31.53	8.54	8.61
4	0.1	0.001	1.0	1.0	46.52	9.55	9.57
5	0.05	0.049	1.0	1.0	20.20	3.72	3.81
6	0.05	0.01	1.0	1.0	40.24	6.69	6.76
7	0.05	0.005	1.0	1.0	51.17	7.74	7.79
8	0.05	0.001	1.0	1.0	79.84	9.23	9.25

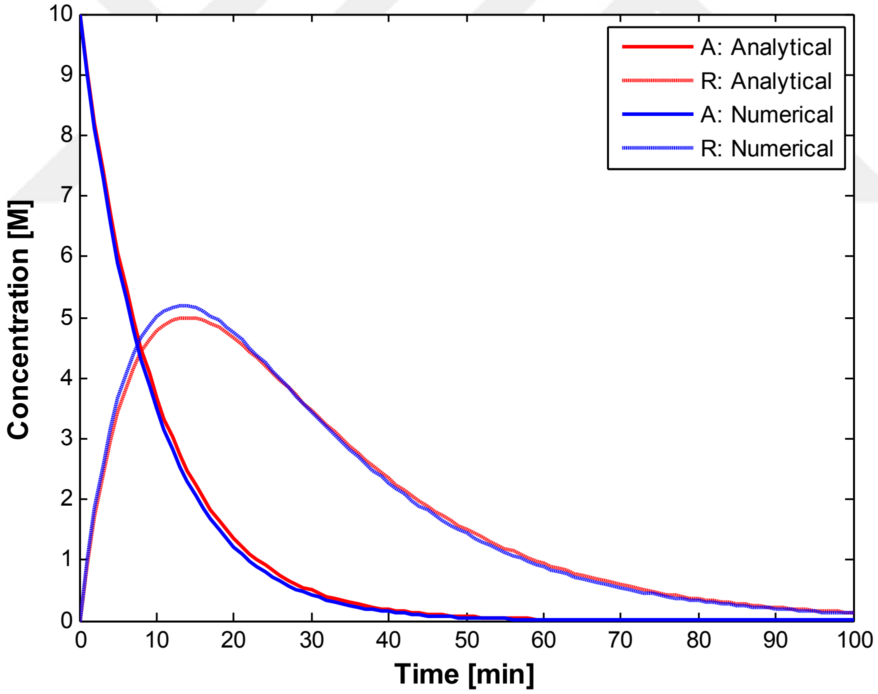


Figure 4.1 Concentration profile with $k_1 = 0.1\ \text{min}^{-1}$ and $k_2 = 0.05\ \text{min}^{-1}$.

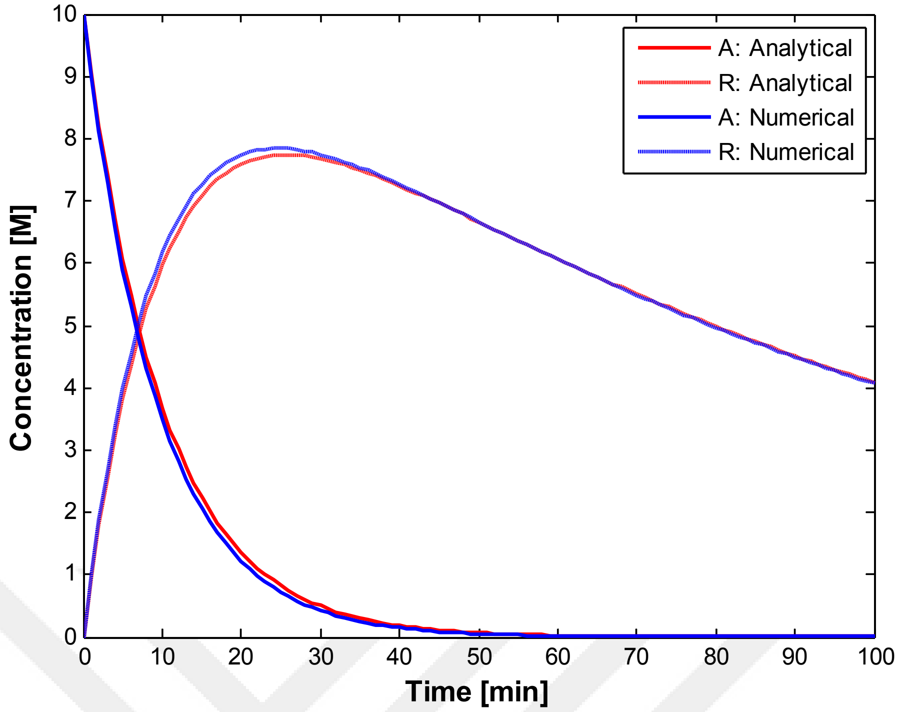


Figure 4.2 Concentration profile with $k_1 = 0.1\ \text{min}^{-1}$ and $k_2 = 0.01\ \text{min}^{-1}$.

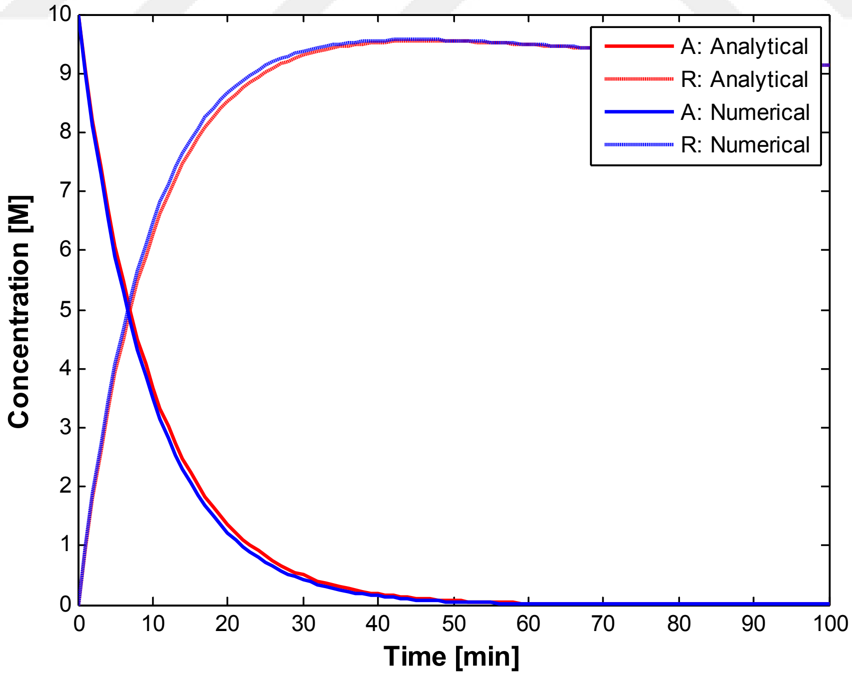


Figure 4.3 Concentration profile with $k_1 = 0.1\ \text{min}^{-1}$ and $k_2 = 0.001\ \text{min}^{-1}$.

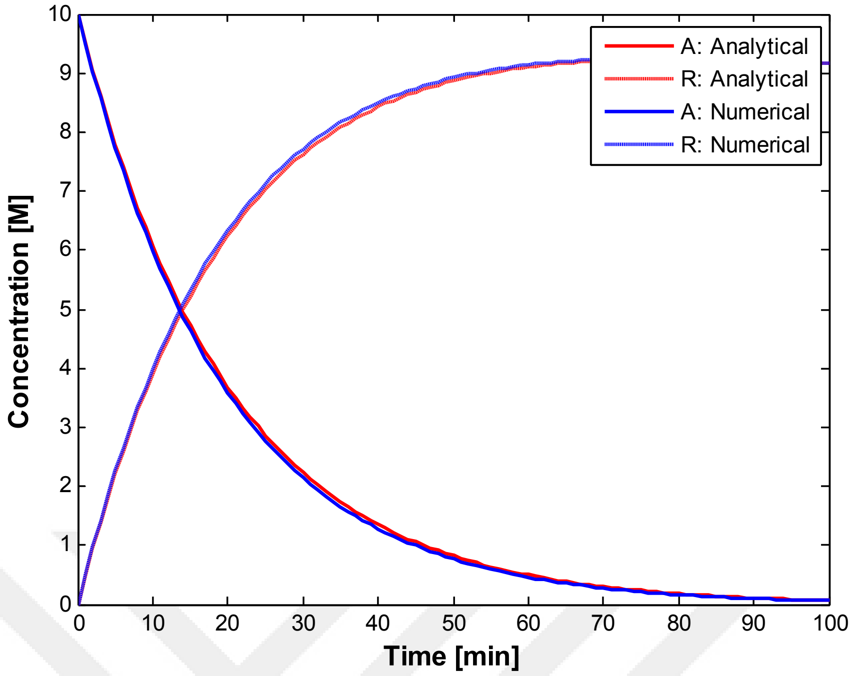


Figure 4.4 Concentration profile with $k_1 = 0.05$ min^{-1} and $k_2 = 0.001$ min^{-1}.

Figures 4.1, 4.2, 4.3 and 4.4 represent the most typical trials among all of the combinations of different first and second reaction rate constants. As the reaction rate constants change, the optimal time changes accordingly. Generally, it can be stated that as the rate constants decrease, the optimal time is achieved later, thus the conversion of R to S is delayed.

Among all of the trials, the maximum concentration of R, which is the desired product in this reaction, is achieved at the rate constants of $k_1 = 0.1$ min^{-1} and $k_2 = 0.001$ min^{-1} with a value of 9.55 L/mol for analytical method and 9.57 L/mol for numerical method. Considering the conditions, the most optimal trial is where the optimal time is 46.5 minutes and where the concentration is maximum. However, in order to see the further minimum values for R during the reaction, 0.05 min^{-1} and 0.01 min^{-1} are chosen for the rate constants respectively.

Table 4.2 Optimal time due to various increments.

Trial	k_1 (1/min)	k_2 (1/min)	dt (Ana)	dt (Num)	t_{opt} (min)	C_{Rmax} (Ana)	C_{Rmax} (Num)
1	0.05	0.01	10.0	10.0	40.24	6.69	7.55
2	0.05	0.01	10.0	5.0	40.24	6.69	7.06
3	0.05	0.01	10.0	1.0	40.24	6.69	6.76
4	0.05	0.01	10.0	0.5	40.24	6.69	6.72
5	0.05	0.01	15.0	10.0	40.24	6.65	7.55
6	0.05	0.01	20.0	10.0	40.24	6.69	7.55
7	0.05	0.01	25.0	10.0	40.24	6.56	7.55

Table 4.2 was prepared to show the effect of the numerical time increment on the results such as the optimal time and maximum concentration of R. Therefore the reaction rate constants k_1 and k_2 were kept constant for various values of the numerical and analytical time increments. It can be seen that the maximum concentration of R is much less than the ones obtained with 1.0 min^{-1} values of dt intervals. These values were chosen on purpose to prove that when the increments are smaller, the control over the reaction is better and the analytical and numerical values are similar. Besides, the obvious difference between the curves can be seen. When the increments are larger, the edges of the curve are larger, it is because of that the larger the increments, the less parts the curve is divided into. As a result, the smaller the increments, the better the values for the analytical and numerical methods.

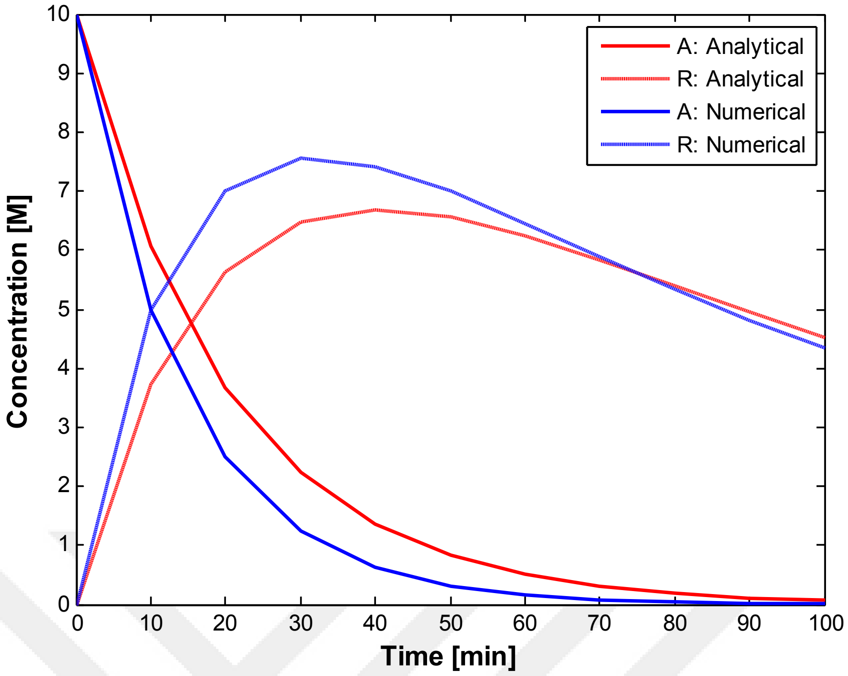


Figure 4.5 Concentration profile with dt(a) = 10.0 minutes and dt(n) = 10.0 minutes

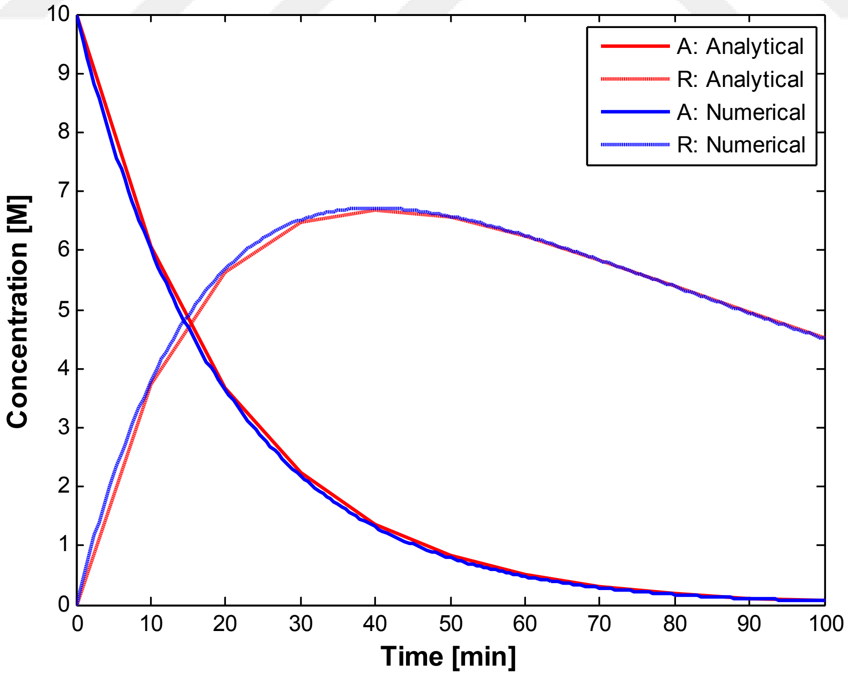


Figure 4.6 Concentration profile with dt(a) = 10.0 minutes and dt(n) = 0.5 minutes

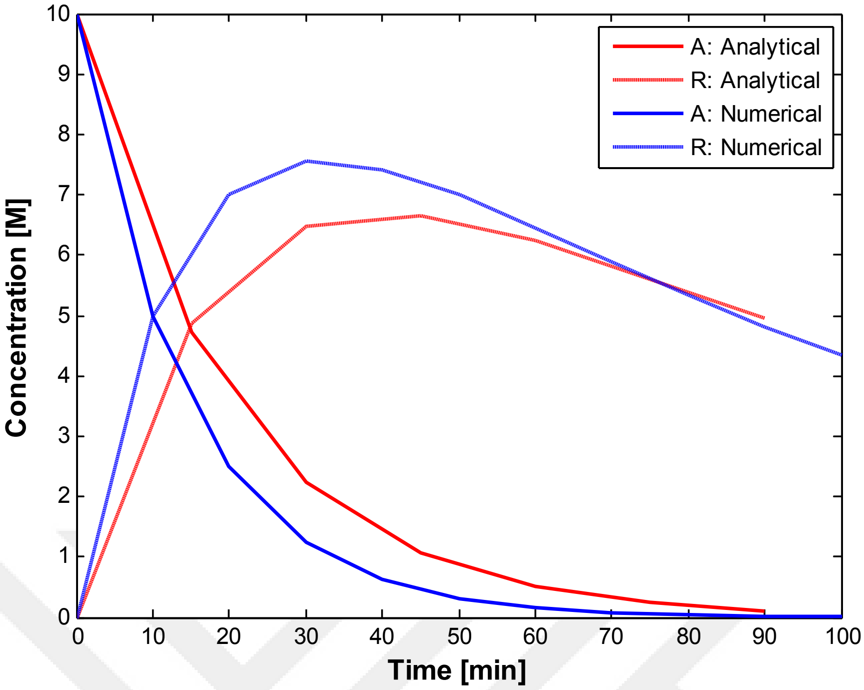


Figure 4.7 Concentration profile with dt(a) = 15.0 minutes and dt(n) = 10.0 minutes

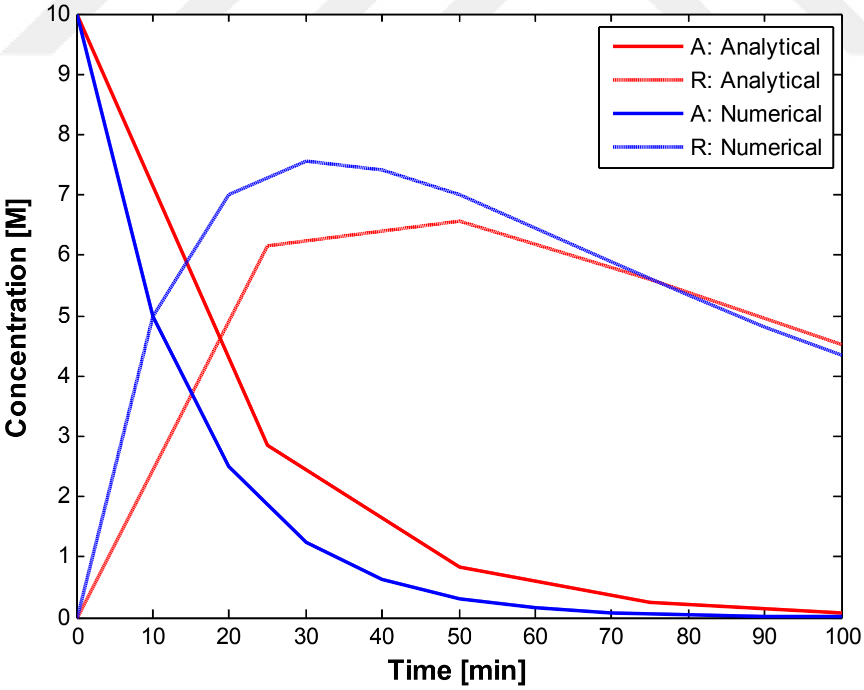


Figure 4.8 Concentration profile with dt(a) = 25.0 minutes and dt(n) = 10.0 minutes

Figures 4.5, 4.6, 4.7 and 4.8 represent the most typical trials among all of the combinations of different numerical and analytical time increments. As the analytical and numerical time increments change, the curves of analytical and numerical methods change accordingly. Generally, it can be stated that as the difference between analytical and numerical time increments increases, the difference between the profiles increase. As a result, using smaller numerical time increments is better for achieving better yield of the desired product.

4.1.2. Semi-Batch Reactor

An isothermal semi-batch reactor with second order will be processed. Assuming a production of a chemical substance which is an irreversible liquid-phase reaction, the elementary rate law is followed. The reaction can be expressed as follows (Fogler, 2006):

$$A + B \rightarrow C \rightarrow D$$

An aqueous solution of B will be fed to the reactor at a constant volumetric rate, where the aqueous solution of A is placed in the reactor initially. The reaction rate constant does not depend on temperature. Therefore, the value is constant for the specific reaction. The following equations will be used in order to build up the optimization program, for numerical solution.

$$r_A = -kC_AC_B \tag{4.1}$$

$$\frac{dC_A}{dt} = -kC_AC_B - \frac{v_o}{V}C_A \tag{4.2}$$

$$\frac{dC_B}{dt} = -kC_AC_B + \frac{v_o}{V}(C_{Bo} - C_B) \tag{4.3}$$

$$V = V_o + v_o t \tag{4.4}$$

$$\frac{dC_C}{dt} = kC_AC_B - \frac{v_oC_C}{V} \tag{4.5}$$

$$X = \frac{C_{Ao}V_o - C_AV}{C_{Ao}V_o} \tag{4.6}$$

The optimum temperature profile and the concentration change of the reactants are represented below, obtained by numerical solution using EM.

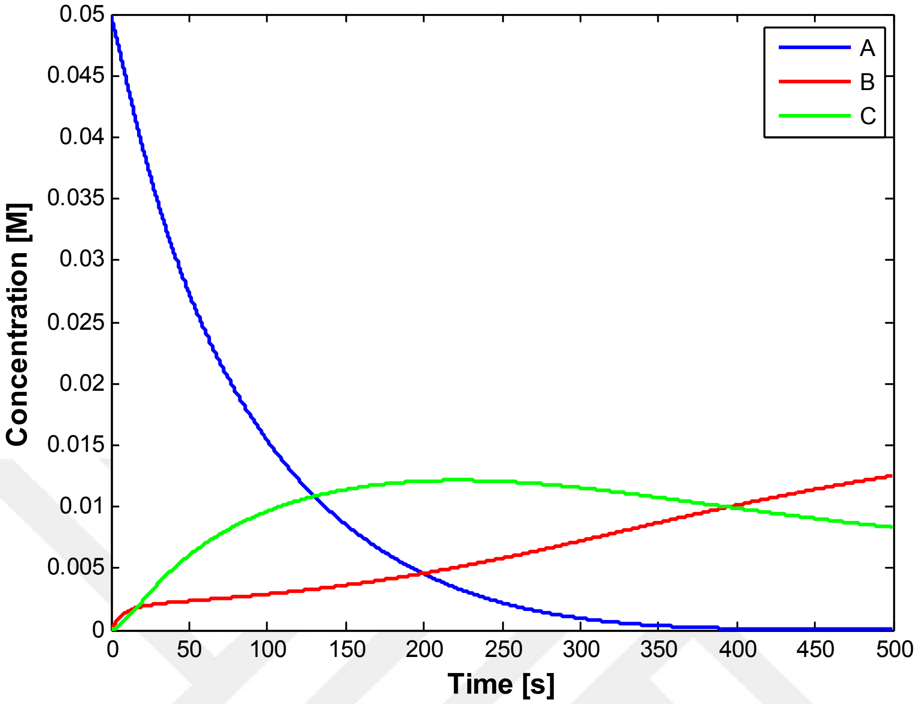
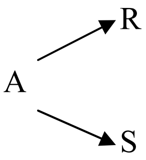


Figure 4.9 Concentration profile for an isothermal semi-batch reactor.

In the overall reaction, C is the desired product rather than D. Therefore, D is not included in the equations and its concentration profile was not presented in Figure 4.9. Since this reaction is isothermal, the temperature is constant; therefore the best yield of the desired product can be obtained by controlling the initial concentrations. As a result, optimization of isothermal processes is not a complicated procedure.

4.2. Optimization for Nonisothermal Reactors

4.2.1. Batch Reactor



The above mentioned parallel reaction is the main reaction for the following example.

Parallel Reaction in a Batch Reactor

The problem for the below given algorithm is referenced from Himmelblau and Edgar, 2001. The parallel reaction takes place in a batch reactor. The desired product is B and the objective is to find the temperature profile for the maximum concentration of B. The initial conditions, activation energies and gas constant are given before running the main program. By the optimal functions and iterations, the optimal time and temperature profile is obtained. For the real life reactions such as industrial batch processes, the relevant technique can be used to achieve the optimal temperature profile of a desired product. The following graphs show that the optimal concentration and temperature profile could be achieved at a very short interval.

Case 1:

$$A \xrightarrow{k_1 > k_2} R \text{ (With lower activation energy)}$$

$$A \xrightarrow{k_1 > k_2} S \text{ (With higher activation energy)}$$

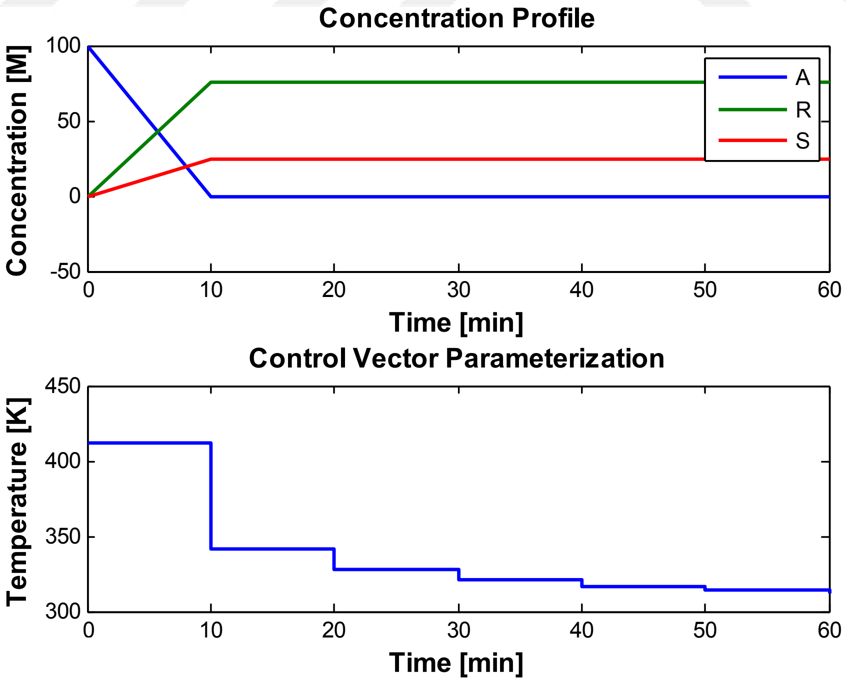


Figure 4.10 Concentration-temperature profiles for a parallel reaction in a batch reactor (dt = 10 minutes)

For Fig. 4.10, the optimal temperature profile and the maximum concentration of R have been achieved by changing the temperature profile at 10 minute intervals. However, in order to control this reaction, it has taken a long time to iterate the conditions.

The temperature range is constrained between 300 K and 450 K. It can be seen from the figures that the optimal time and maximum concentration can be obtained even in 5 minutes, however in order to achieve this profile, it takes a lot of time to iterate until the reactor proceeds with the optimal conditions. Considering these two conditions, when dt is 5 minutes, it takes lesser time to achieve the optimal conditions.

Case 2:

$$A \xrightarrow{k_1>k_2} R \text{ (With lower activation energy)}$$

$$A \xrightarrow{k_1>k_2} S \text{ (With higher activation energy)}$$

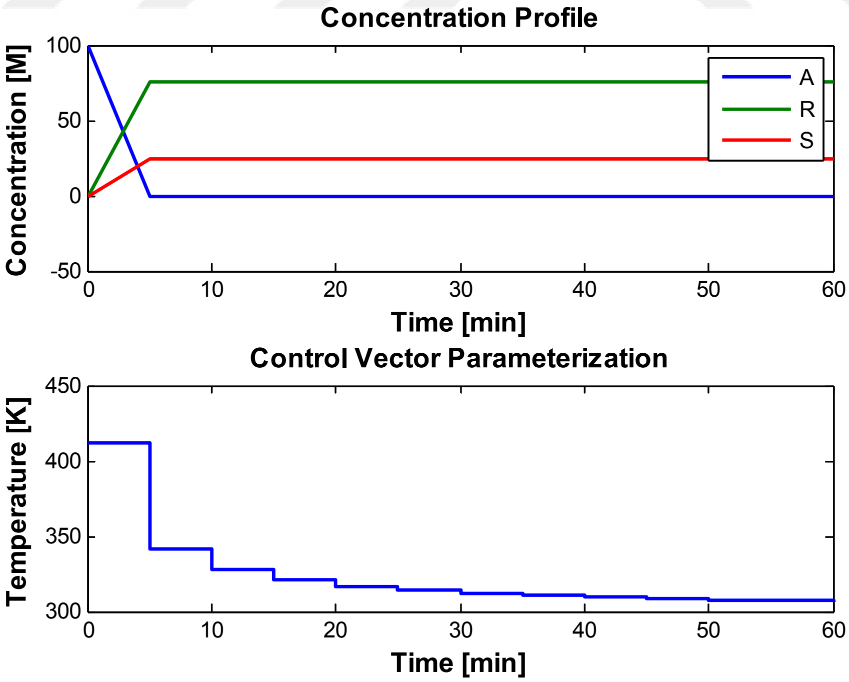


Figure 4.11 Concentration-temperature profiles for a parallel reaction in a batch reactor (dt = 5 minutes)

From the above given figures, it can be concluded that when the first reaction has a lower activation energy and thus a higher rate constant, the optimal time for the maximum R is achieved very quickly. Besides this condition shows the quicker optimum time for the reaction to achieve the maximum concentration for R, it is not suitable for a real life reaction. Also, since R is the desired product and when all the parameters are all in favor with a maximum R concentration, the functionality of the optimization is meaningless. Changing the parameters will give the following figures with results close to real life reaction conditions.

In the given algorithm, optimal function F is obtained by a spatial function in Matlab®. Considering the nature of Matlab, every function is calculated as a minimum. Therefore, in order to calculate the maximum point of a function in Matlab, negative of the function should be found. Regarding the algorithm, at the step where G1 function is equalized to –F, which is the optimal function, if they are not equal, the route goes back to the step where the optimal function is found.

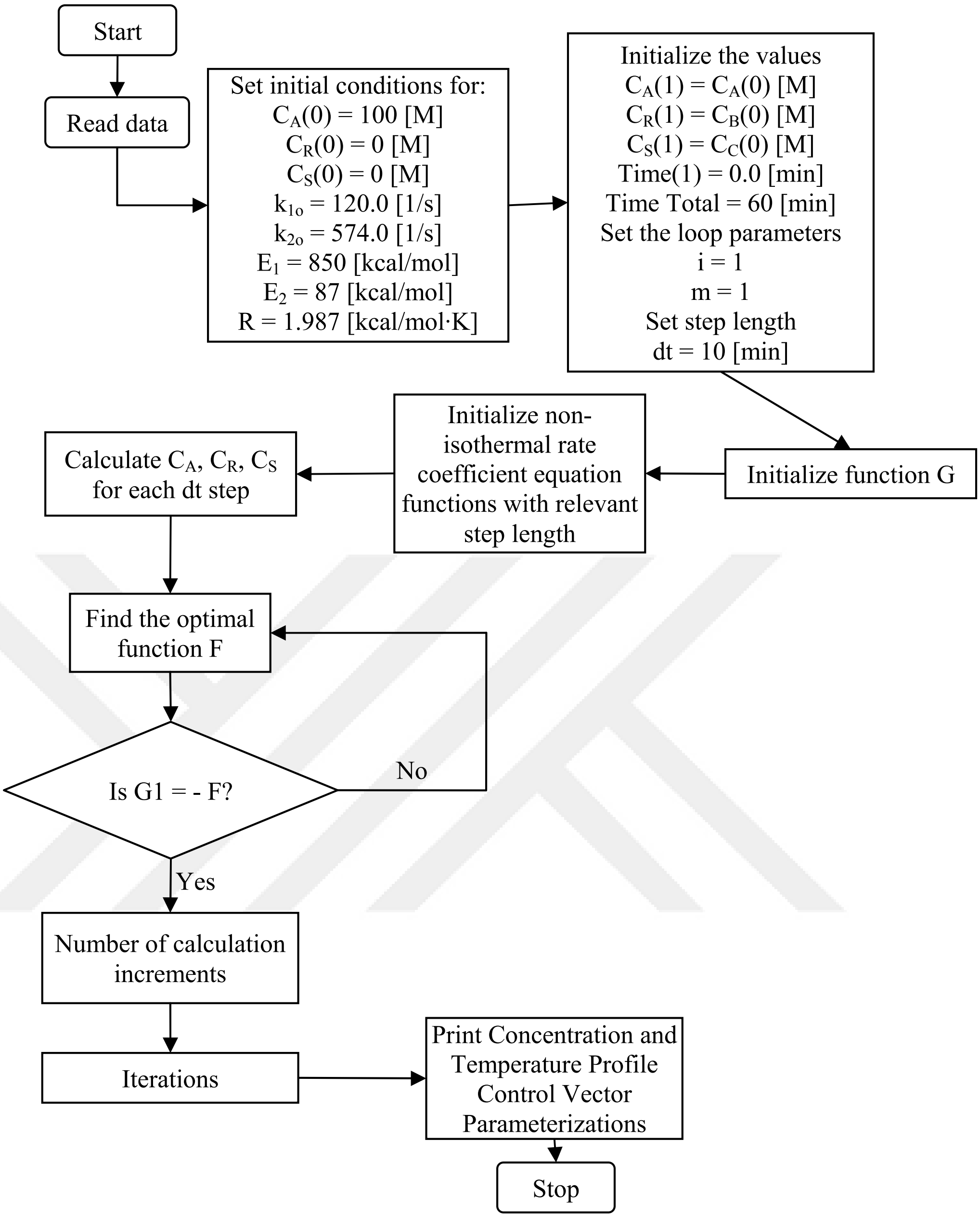


Figure 4.12 Algorithm for the parallel reaction in a batch reactor optimization.

Since the previously mentioned reaction occurred with a faster first reaction and a slower second reaction, the optimization was easy to perform. However, when the second reaction rate constant is higher and the activation energy is lower than the first reaction, the general reaction is in favor with undesired product S. Reactant A tends to converge into S more than R. On the other hand, since R is the desired product with higher activation energy and a lower reaction rate constant, the optimization program tends to favor the reaction into the pathway of producing R. It can be seen from the figures that as the reaction continues, S is kept at a minimum concentration and R is obtained at a maximum concentration with an increasing temperature profile. This means that in order to obtain a high concentration of R with higher activation energy and lower rate constant for R, the temperature should be gradually increased for relevant time intervals with the indicated temperatures.

Case 3:

$$A \xrightarrow{k_1<k_2} R \text{ (With higher activation energy)}$$

$$A \xrightarrow{k_1<k_2} S \text{ (With lower activation energy)}$$

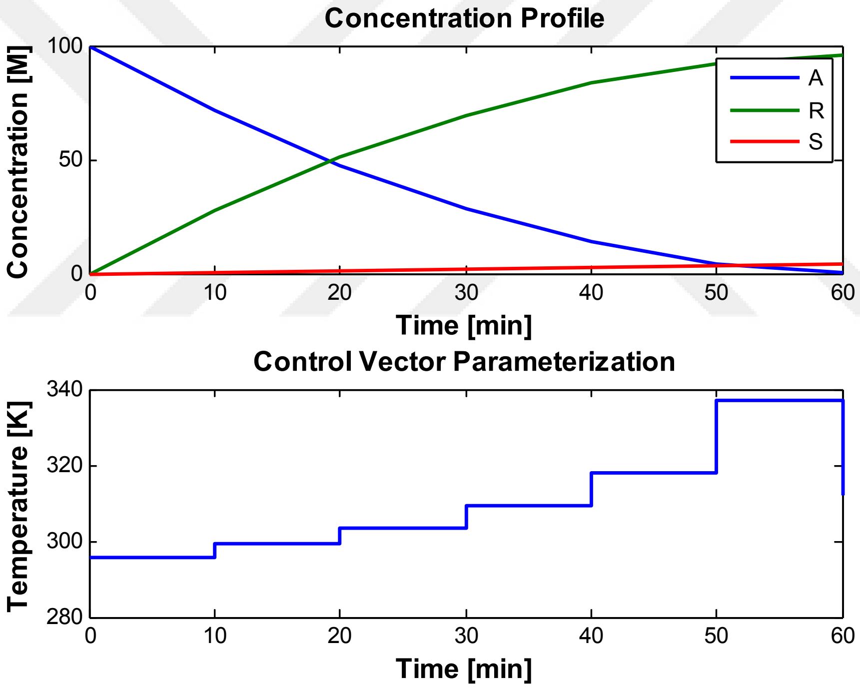


Figure 4.13 Concentration-temperature profiles for a parallel reaction in a batch reactor (dt = 10 minutes)

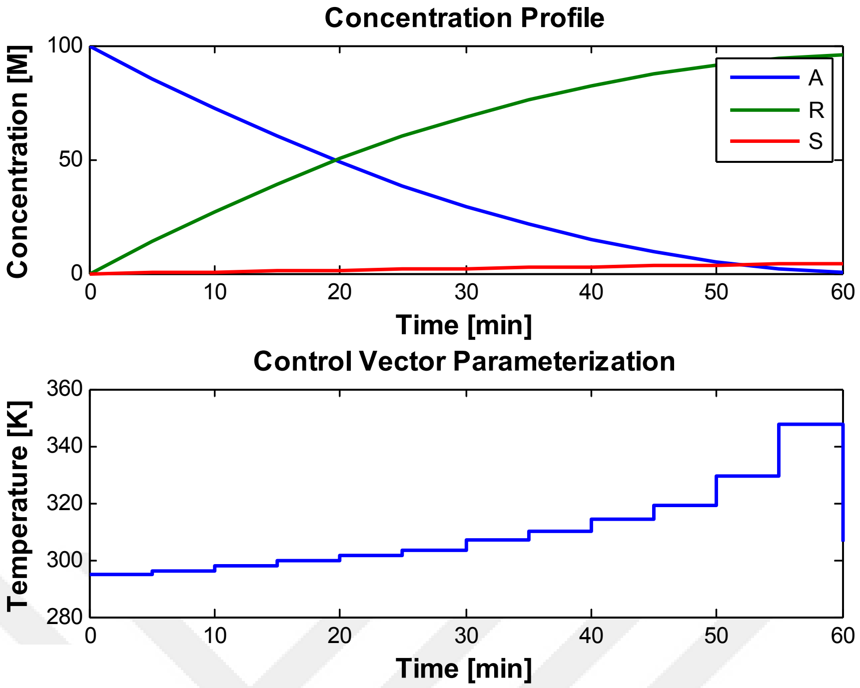


Figure 4.14 Concentration-temperature profiles for a parallel reaction in a batch reactor (dt = 5 minutes)

Series Reaction in a Batch Reactor (Jensen and Jeffreys, 1977)

The series chemical reaction A → R → S is to be carried out. All the reactions are first order and the rate constants are related to temperature through the Arrhenius Law. In order to derive the set of equations to evaluate the temperature profile that will maximize the production of the desired product R, the equations for the solution of problem are given in the Appendix D. The concentration profile for the reaction is shown in the following figure. Since the product S is an undesired product, it hasn't been indicated in Fig. 4.15.

Recalling from the previous examples, A is converted to R and R is converted to S according to the rate of the reactions. Even if the reaction between R and S is very slow, there is still a conversion from R to S. In order to evaluate the reactions close to real life processes, reaction rates of the two consecutive reactions have been taken closely. Also the activation energies for both of the reactions have been chosen similar. Concentration profile, optimum temperature profile, temperatures after each iteration, relationship between temperature, iteration number and time, relationship between dH/dT, temperature and time and finally the comparative profile between three different initial temperature have been indicated in the following figures. Before any discussion, it would be appropriate to explain dH/dT. The Hamiltonian expression (dH/dT) is the objective function (Hamiltonian) with respect to temperature which is the optimization variable.

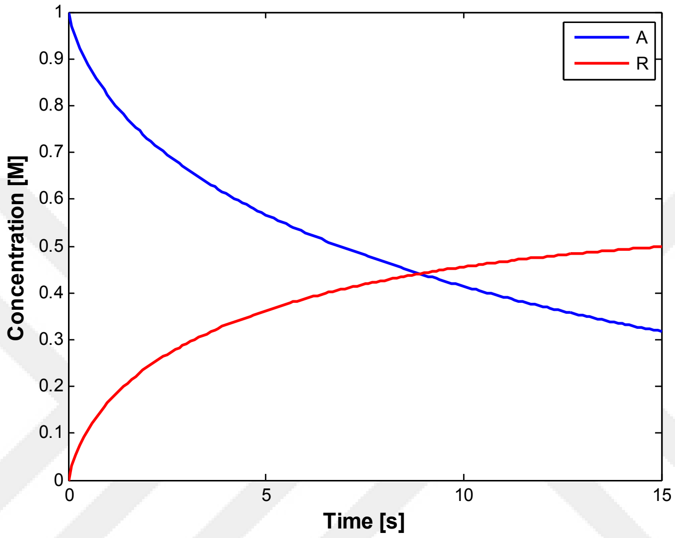


Figure 4.15 Concentration profile of the series reaction.

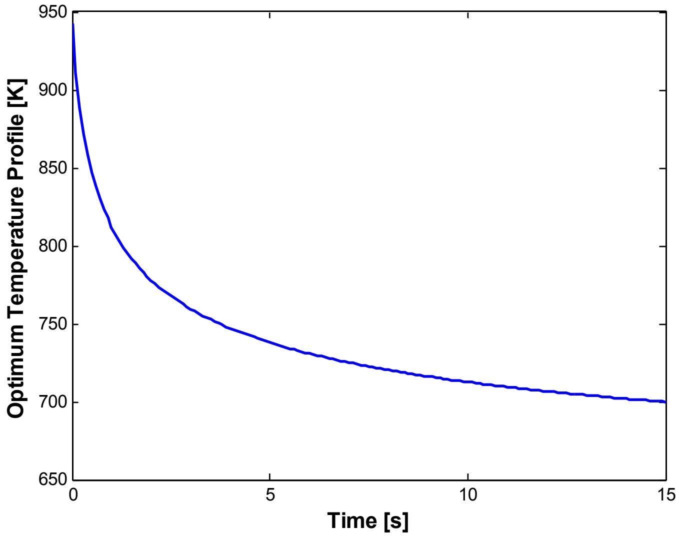


Figure 4.16 Optimum temperature profile of the reaction.

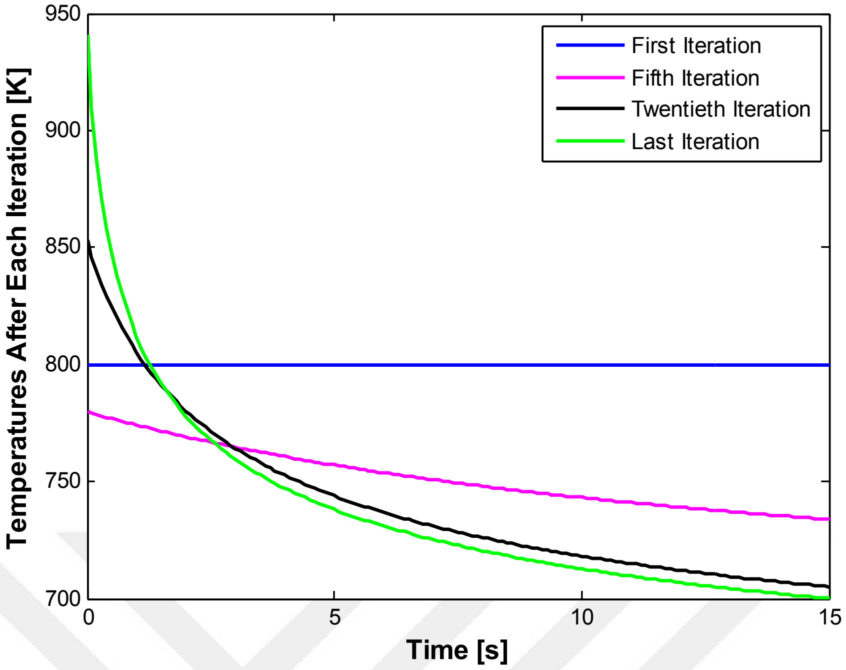


Figure 4.17 Temperatures after each iteration during whole reaction.

Since the number of iterations is very large to be included in the above given Fig. 4.17, four main iterations are represented. As the iterations increase up to the last iteration, the temperature profiles gradually become curves and the results of the last iteration give the optimum profile, Fig. 4.16.

The given figures 4.18 and 4.19, represent the results obtained after each iteration for the temperature profile and the temperature derivative of Hamiltonian, dH/dT. Here, dH/dT is the derivative gradient of Hamiltonian expression to the temperature which is supposed to be very close to zero when the optimum is reached. The relation for dH/dT is defined by the equations given in Appendix D, between temperature, time, concentration, activation energies and the rate constants.

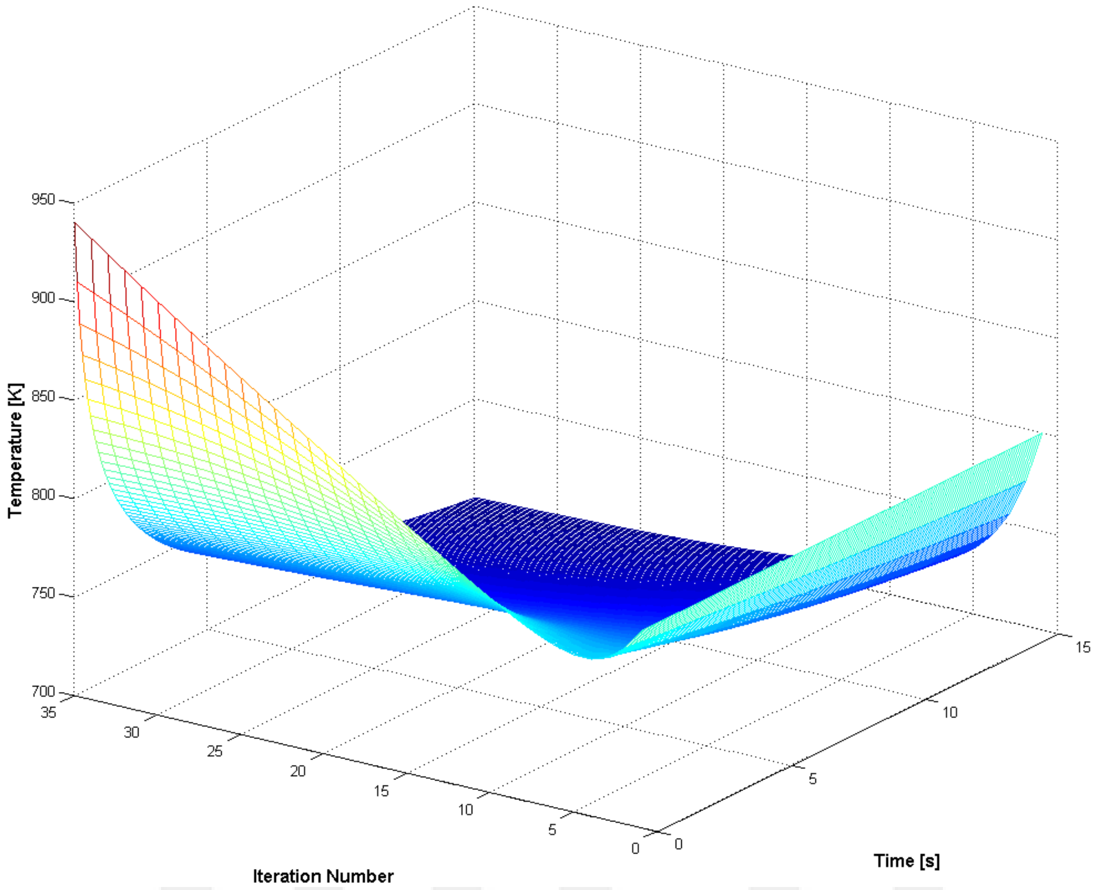


Figure 4.18 The relationship between iteration number, temperature and time.

As a result, for the relevant reaction, the initial temperatures were tried to be 900 K, 450 K and 400 K in Fig. 4.20. By the following algorithm in Fig. 4.21 for the optimization in Fig. 4.20, the relevant temperature profiles have been obtained for the 3 proposed constant initial temperatures guesses. At the end of the optimization for each temperature guess, the final and optimal temperatures and the profile pathways are the same. However, the iteration number and the time to optimize differ. Minimum iteration number is obtained at an initial temperature of 800 K. The relation between three different initial temperatures is given in Fig. 4.20. Whatever the initial guess for the temperature profile is, either 400 or 900 K, the same final and optimal temperature profiles are achieved at different iterations for a computation time of 15 seconds in order to maximize the concentration of R.

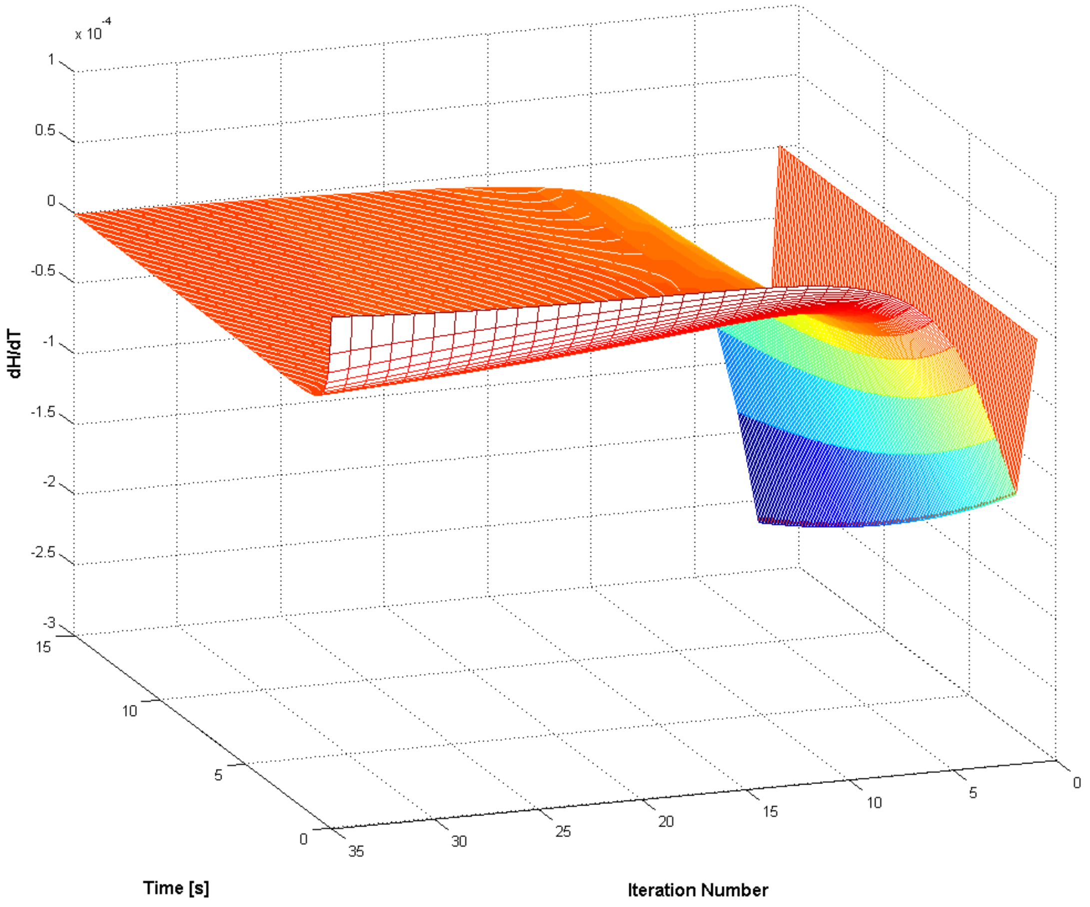


Figure 4.19 The relationship between iteration number, dH/dT and time.

For this kind of problem, there are many parameters that can be controlled and changed depending on the objective function stating the desired objective. However, in all engineering problems and in real life, the most common idea is to obtain the maximum yield with appropriate quality, minimum cost for the process, optimal working conditions for the equipment to not to fail early, in other words depreciation. In this process, the objective function is to obtain the maximum concentration of R, without converging into too much S.

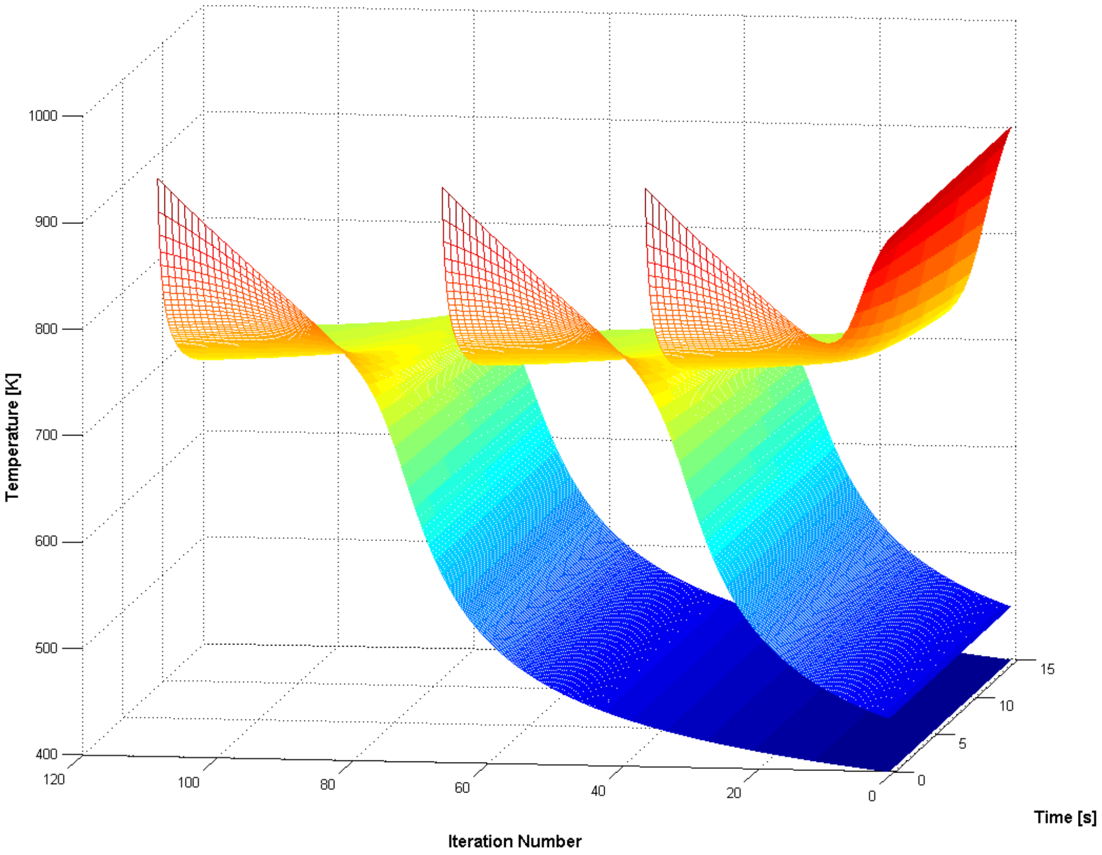


Figure 4.20 The relationship between iteration number, temperature profile and time for three different initial temperatures.

Inequality constraints are the temperature range limit, which is between 400 K and 900 K. According to these values, the algorithm to solve the model equations and to realize the optimization was programmed using Matlab®. The iterative algorithm used for optimization is presented in Fig. 4.21. Optimization of a series reaction of a batch process can be performed by trajectory optimization. Trajectory optimization is the process of designing a trajectory that minimizes or maximizes some measure of performance within prescribed constraint boundaries. Most of the time, trajectory optimization is used in aerospace field. However, with appropriate techniques, this optimization can be used in chemical engineering processes.

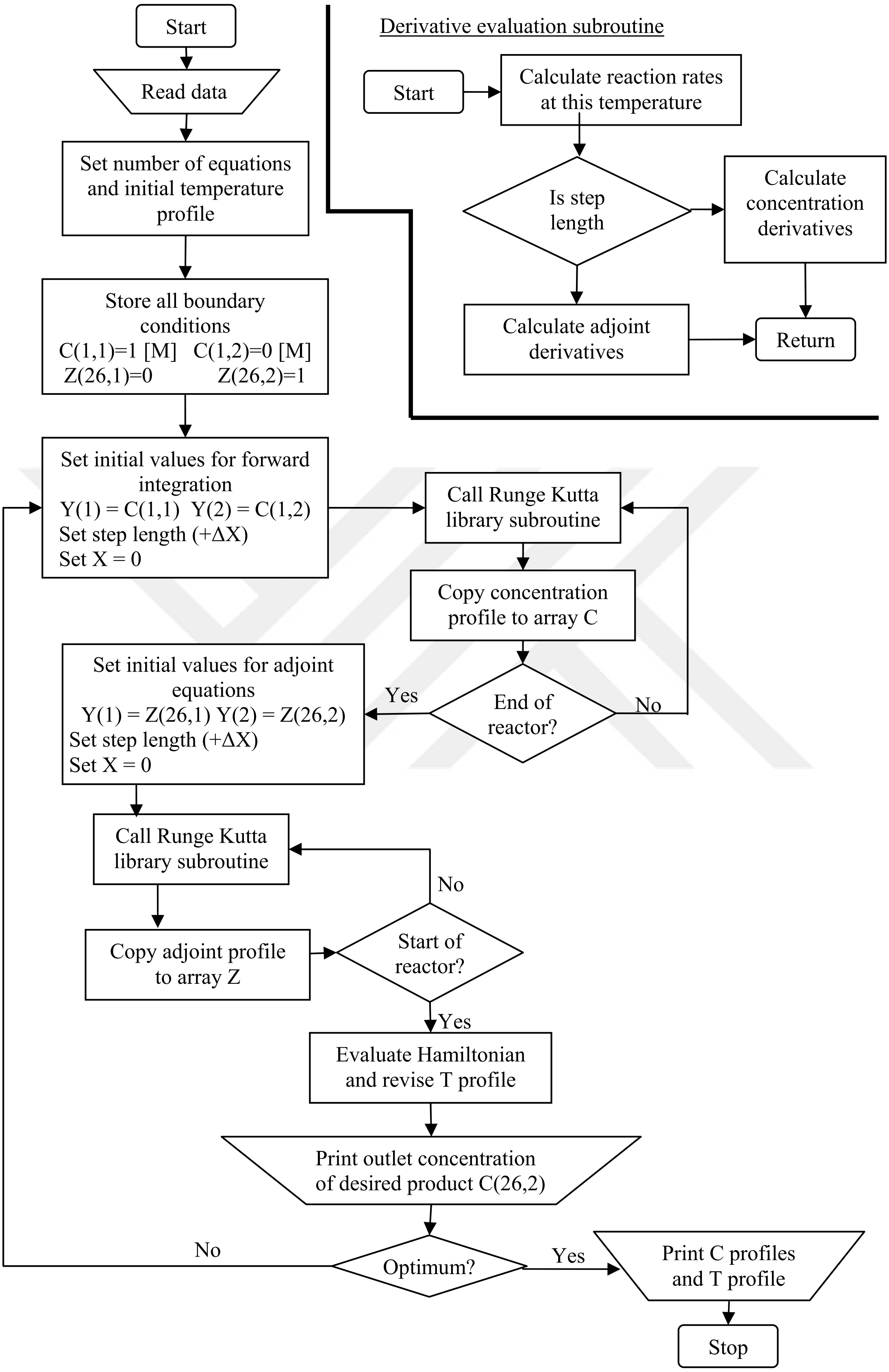


Figure 4.21 Algorithm for the series batch reactor optimization (Jensen et al, 1977)

4.2.2. Semi-Batch Reactor

Regarding the nature of semi-batch operations, they are usually conducted in a stirred vessel. One of the reactants is loaded into the vessel as a single charge and the other added gradually. In an another case of a semi-batch reactor, all the reactants are placed in a reactor and as reaction proceeds, one of the products is continuously removed, such as some esterification reactions and the boiling of water. Optimization of semi-batch reactors are almost as the same as batch reactors. The only difference is that the material balance equations have to be arranged in accordance with material withdrawals or additions. According to these withdrawals or additions, the pathway for the optimization can be generalized.

(i) The increment size should be chosen. (Δt)

(ii) Starting from the initial temperature T_o and $t = 0$, Δt_1 should be calculated. The calculation should be done for the first time increment Δt, assuming the rate (r) to be that corresponding to the temperature at the beginning of the increment.

(iii) The first estimate of the temperature at the end of the increment T_1 is obtained from the energy balance equation.

(iv) This estimation is used to obtain the rate at the end of the increment (r_1).

(v) The formula $\frac{1}{2}(r + r_1)$ is used to calculate a revised value of Δt_1 and hence for a revised value of T_1.

(vi) This procedure has to be continued until two successive estimates of T_1 are sufficiently close.

(vii) Finally, the next increment is taken and the calculation is repeated until the required degree of conversion is achieved (Compton and Bamford, 1985).

Considering the below mentioned multiple reaction in a semi-batch reactor, with the following parameters, the optimal temperature and concentration change with time will be explained.

$$2A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} 3C$$

The series reactions are catalyzed by a catalyst. All reactions are assumed to be first order in the reactant concentration. The reaction is to be carried out in a semi-batch reactor with a heat exchanger. While pure A enters the reactor at a constant volumetric rate with a constant temperature, initially there is a mixture in the reactor which contains A and catalyst. The reaction rate is assumed to be independent of catalyst concentration (Fogler, 2006).

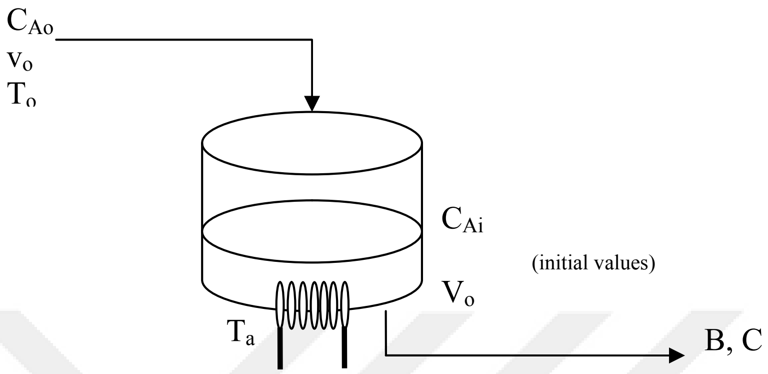


Figure 4.22 Semi-batch reactor with a heat exchanger.

The following mole balances and rate laws will be used for the optimization of the reaction.

$$\frac{dC_A}{dt} = r_A + \frac{(C_{Ao} - C_A)}{V} v_o \tag{4.7}$$

$$\frac{dC_B}{dt} = r_B - \frac{C_B}{V} v_o \tag{4.8}$$

$$\frac{dC_C}{dt} = r_C - \frac{C_C}{V} v_o \tag{4.9}$$

$$r_A = -k_1 C_A \tag{4.10}$$

$$r_B = -k_2 C_B \tag{4.11}$$

$$V = V_o + v_o t \tag{4.4}$$

The above given equations will be used in order to create the program. However, there should be an energy balance equation which must include the reaction energies and the temperature of the heat exchanger T_a (or the heat exchange rate between the reacting fluid and heat exchanger). Reaction rate constants are temperature dependent. Therefore Arrhenius equations will be used as presented before. C_p are the heat capacities of each reactant.

$$\frac{dT}{dt}=\frac{UA(T_a-T)-F_{Ao}C_{P_A}(T-T_o)+[(\Delta H_{RxA})(r_A)+(\Delta H_{RxB})(r_B)]V}{\left[C_A C_{P_A}+C_B C_{P_B}+C_C C_{P_C}\right]V+N_{catalyst}C_{P_{catalyst}}} \tag{4.12}$$

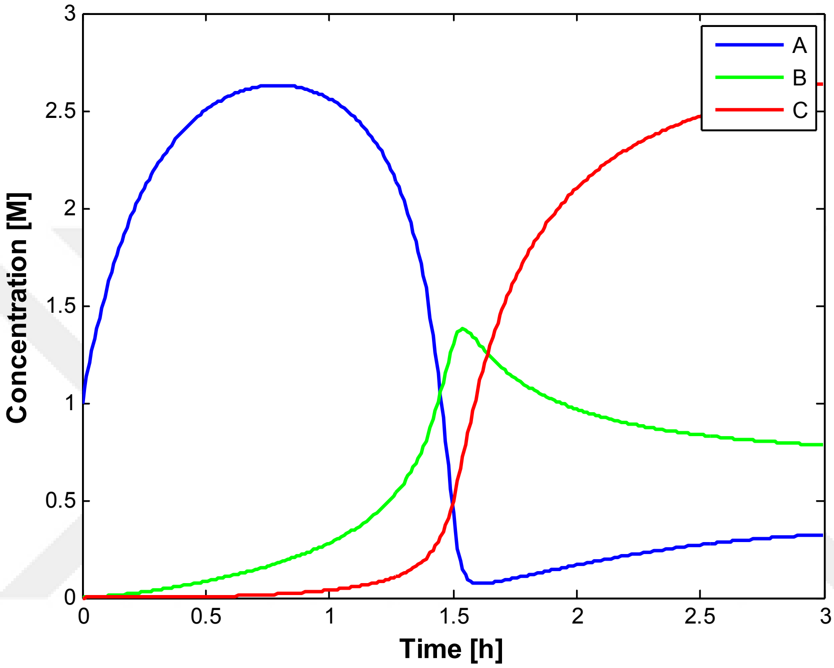


Figure 4.23 Concentration change with time.

Figure 4.23 gives the optimal time to end the process. At 1.5 hour of process, the reaction should be stopped in order to obtain the best yield of the desired product B. While the concentration of B increases until 1.5 h, the optimal temperature profile should be as given in Figure 4.24. Since the reaction carried out is an endothermic reaction, temperature is raised until B concentration is maximum when the time is 1.54 h. At the very same point, the maximum temperature is 446.4 K. The maximum B concentration obtained is 1.38 mol/L. The reaction could be carried out until 1.64 h, where C concentration overshoots B concentration. However, the reaction should not be continued after 1.64 hours, because C concentration will be higher than that of B and it is inevitable to obtain higher C concentrations for times further than 1.64 h. When the reaction is continued for 6 hours, C concentration inevitably and quickly rises where the concentration of B decreases. The temperature could be decreased but this will result in a less B concentration.

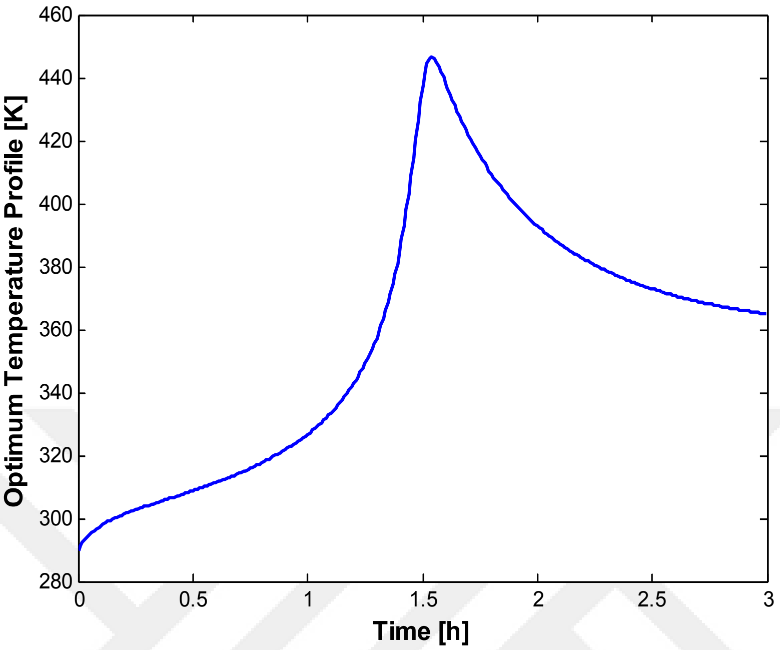


Figure 4.24 Optimum temperature profile.

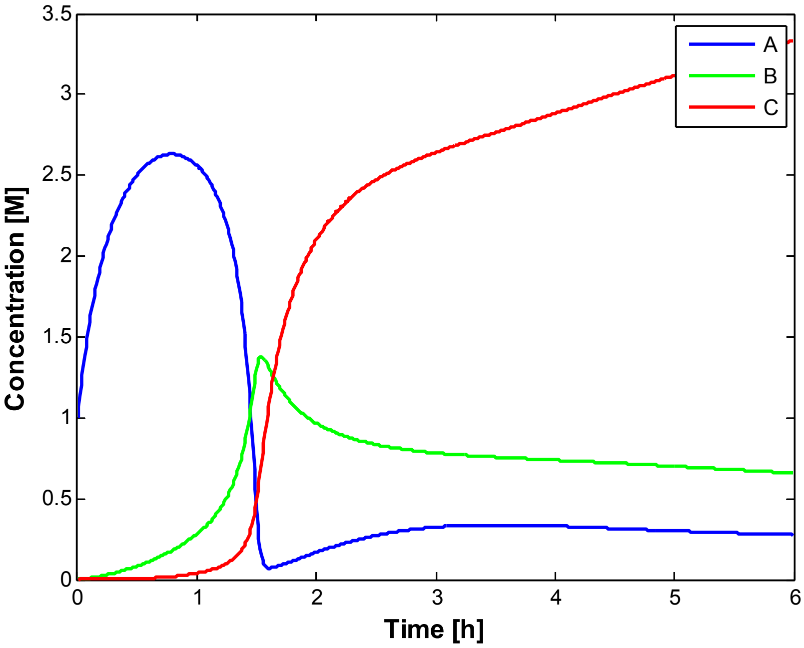


Figure 4.25 Nonisothermal reaction carried out for 6 hours.

Chapter 5

5. Conclusion and Future Suggestions

Among all of the results and discussions given, it shouldn't be forgotten that, while integrating these optimization techniques to real life processes, the reaction time will be longer in order to achieve the desired yield or other desired properties. Furthermore, the reaction rates and the order of the reactions will differ. If the parameters, manipulated and controlled variables are chosen well, this trajectory optimization technique can be used in all optimization problems in engineering and real life processes.

Thinking of the real life manufacturing industry, time, costs, and product quality are the most important constraints. Generally all engineers try to perform the optimizations for the manufacturing with an aim of the least time, the best product quality with a least cost. The most intriguing and also the most complicated part of these optimizations is to find the optimal combinations of these conditions. Some processes can yield best products in a long time of reaction while some other processes can yield best products in an optimal time but they can be very expensive. This expensiveness can force the purchasing power of the buyers. Furthermore, sometimes because of the process type, the temperature cannot be controlled. Even if the "best" optimization cannot be achieved, the nearest optimization techniques to be applied into real life processes can be found.

Batch and semi batch processes exist in a wide variety of designs in industry. In this study, for the optimization of batch and semi batch processes, CVI and trajectory optimization have been discussed. The pathways, algorithms for optimizations regarding batch processes like pharmaceuticals, food industries and regarding semi batch processes like fermentation, thermochemical heat storage unit, have been given.

In this study, model based optimization methods were represented systematically, from the simplest process to the most complicated process. The results for these processes were given and discussed. No matter how complicated the process is, or no matter how advanced the model is, a system can be divided into subprocesses and can be optimized by the approaches discussed in this study. The important thing is to know the whole process and the subprocesses. Besides the knowledge of the process and the subprocesses, the model equations, constraints and objective function should be defined in a detailed way.

CVI and trajectory optimization techniques which were discussed in this study, can be performed in real life industry processes. By using these techniques in an industrial scale, the real time optimization of the batch and semi batch processes can be conducted. For future studies, real time values can be substituted into suggested techniques and the optimal yields can be achieved.

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Appendix A

Appendix A-1: Optimization of an Isothermal Series Reaction (n_1,n_2=First order)

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

According to the reaction above, the following reaction rate equations can be written. Note that reaction rate constants do not depend on temperature.

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

Integrating the reaction rate for A, the following equation is obtained.

$$C_A = C_{A_0} e^{-k_1 t}$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

$$\frac{dC_R}{dt} = k_1 C_{A_0} e^{-k_1 t} - k_2 C_R$$

For this kind of differential equations, the first order differential equation integrating factor shown below can be used.

$$\mu(t) = e^{\int k_2 dt} = e^{k_2 t}$$

The whole equation is multiplied by the integrating factor.

$$e^{k_2 t} \frac{dC_R}{dt} + k_2 e^{k_2 t} C_R = k_1 C_{A_0} e^{(k_2 - k_1)t}$$

This kind of equation can be simplified within the rules of derivation. The above mentioned equation expresses the d (u·v) = u·dv + v·du equation. Therefore, u = $e^{k_2 t}$, v = C_R.

$$d(e^{k_2 t} C_R) = k_1 C_{A_0} e^{(k_2 - k_1)t} dt$$

$$\int d(e^{k_2 t} C_R) = \int k_1 C_{A_0} e^{(k_2-k_1)t} dt$$

$$e^{k_2 t} C_R = \frac{k_1 C_{A_0}}{(k_2 - k_1)} e^{(k_2-k_1)t} + I$$

At initial conditions, t = 0 and $C_R = 0$ are used to find I (integration constant).

$$e^{k_2 \cdot 0} \cdot 0 = \frac{k_1 C_{A_0}}{(k_2 - k_1)} e^{(k_2-k_1) \cdot 0} + I$$

$$I = -\frac{k_1 C_{A_0}}{(k_2 - k_1)}$$

$$e^{k_2 t} C_R = \frac{k_1 C_{A_0}}{(k_2 - k_1)} e^{(k_2-k_1)t} - \frac{k_1 C_{A_0}}{(k_2 - k_1)}$$

$$C_R = \frac{k_1 C_{A_0}}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

When C_R is maximum, the derivative of the same point is zero.

$$\frac{dC_R}{dt} = 0$$

$$\frac{dC_R}{dt} = \frac{k_1 C_{A_0}}{(k_2 - k_1)} \{-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\}$$

$$\frac{k_1}{k_2} = \frac{e^{-k_2 t_{opt}}}{e^{-k_1 t_{opt}}} = e^{(k_2-k_1) t_{opt}}$$

In order to find the optimal time expression, take ln of the above mentioned equation.

$$\ln \frac{k_1}{k_2} = (k_2 - k_1) t_{opt}$$

$$t_{opt} = t_{C_{R_{max}}} = \frac{\ln k_1/k_2}{k_2 - k_1}$$

Appendix A-2: Optimization of an Isothermal Series Reaction (n_1=First, n_2=Zero order)

$$A \xrightarrow{k_1, n=1} R \xrightarrow{k_2, n=0} S$$

The first reaction is a first order reaction and the second reaction is a zero order reaction. Therefore the following reaction rate equations can be written. Note that reaction rate constants are constant, which means they do not change with temperature.

$$\frac{dC_A}{dt} = -k_1 C_A, \frac{dC_R}{dt} = k_1 C_A - k_2$$

Integrating the reaction rate for A, the following equation is obtained.

$$C_A = C_{A_0} e^{-k_1 t}$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2$$

$$\frac{dC_R}{dt} = k_1 C_{A_0} e^{-k_1 t} - k_2$$

Integrating the reaction rate equation;

$$C_R = -C_{A_0} e^{-k_1 t} - k_2 t + I$$

At initial conditions, t = 0 and $C_R = 0$;

$$0 = -C_{A_0} e^{-k_1 \cdot 0} - k_2 \cdot 0 + I, I = C_{A_0}$$

$$C_R = -C_{A_0} e^{-k_1 t} - k_2 t + C_{A_0}$$

At maximum C_R, $\frac{dC_R}{dt} = 0$.

$$0 = k_1 C_{A_0} e^{-k_1 t_{opt}} - k_2 \qquad e^{-k_1 t_{opt}} = \frac{k_2}{k_1 C_{A_0}}$$

$$t_{opt} = \ln\left(k_1 C_{A_0}/k_2\right)/k_1$$

Appendix A-3: Optimization of an Isothermal Series Reaction (n_1=Zero, n_2=First order)

$$A \xrightarrow{k_1, n=0} R \xrightarrow{k_2, n=1} S$$

The first reaction is a zero order reaction and the second reaction is a first order reaction. Therefore the following reaction rate equations can be written. Note that reaction rate constants are constant, which means they do not change with temperature (Solution referred by Levenspiel, 1999).

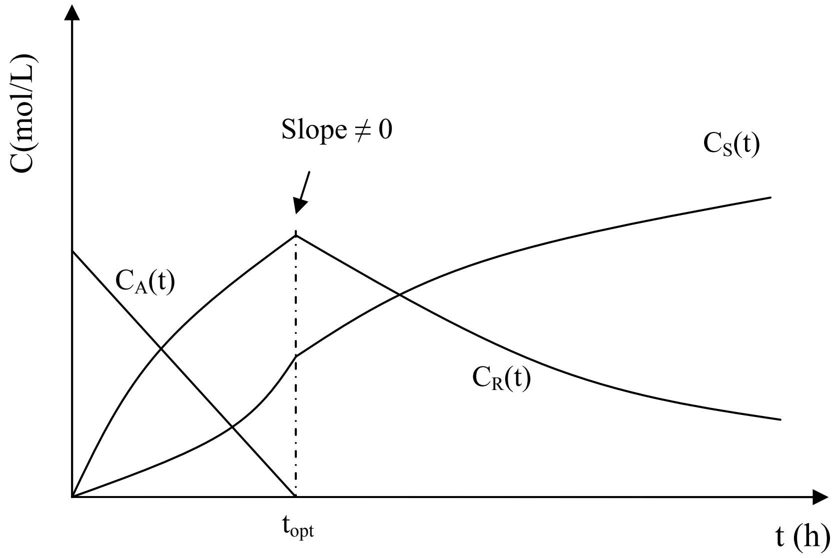
$\frac{dC_A}{dt} = -k_1$ $\qquad$ $\frac{dC_R}{dt} = k_1 - k_2 C_R$

$r_R = k_1 - k_2 C_R$ $\qquad$ $r_R = -k_2 C_R$

$K = \frac{k_2}{k_1/C_{A_0}}$ $\qquad$ $\frac{C_A}{C_{A_0}} = 1 - \frac{k_1 t}{C_{A_0}}$

$\frac{C_A}{C_{A_0}} = \frac{1}{K}(1 - e^{-k_2 t})$ $\qquad$ $t < \frac{C_{A_0}}{k_1}$

$\frac{C_A}{C_{A_0}} = \frac{1}{K}(e^{K-k_2 t} - e^{-k_2 t})$ $\qquad$ $t > \frac{C_{A_0}}{k_1}$



For the optimum time of such reaction, it will be the time when A is fully consumed and converted to R.

Appendix B

Optimization of a Non-isothermal Series Reaction

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

According to the reaction above, the following reaction rate equations and reaction rate coefficient can be written. Note that reaction rate constants depend on temperature.

$$k_1 = \propto_1 e^{-E_1/R_{gas}T(t)}$$

$$k_2 = \propto_2 e^{-E_2/R_{gas}T(t)}$$

$$r_A = \frac{dC_A}{dt} = -\propto_1 e^{-E_1/R_{gas}T(t)} C_A$$

$$r_R = \frac{dC_R}{dt} = \propto_1 e^{-E_1/R_{gas}T(t)} C_A - \propto_2 e^{-E_2/R_{gas}T(t)} C_R$$

In order to continue the dC_A integration, the relationship between T and C_A should be found. Therefore, the energy balance equations are also needed.

$$V \cdot \rho \cdot C_p \cdot \frac{dT(t)}{dt} = -r_A(t)\Delta H_1 - r_R(t)\Delta H_2 - UA\left(T_j - T(t)\right)$$

The above mentioned equation expresses the energy balance of the relevant reactor. However if the material balance equations are submitted into the energy balance equation, since there is a nonlinear term in the equation, the general equation cannot be solved analytically. This kind of complex differential equation can be solved numerically.

Appendix C

Appendix C-1: Optimal time due to various rate constants (Total time = 100 min)

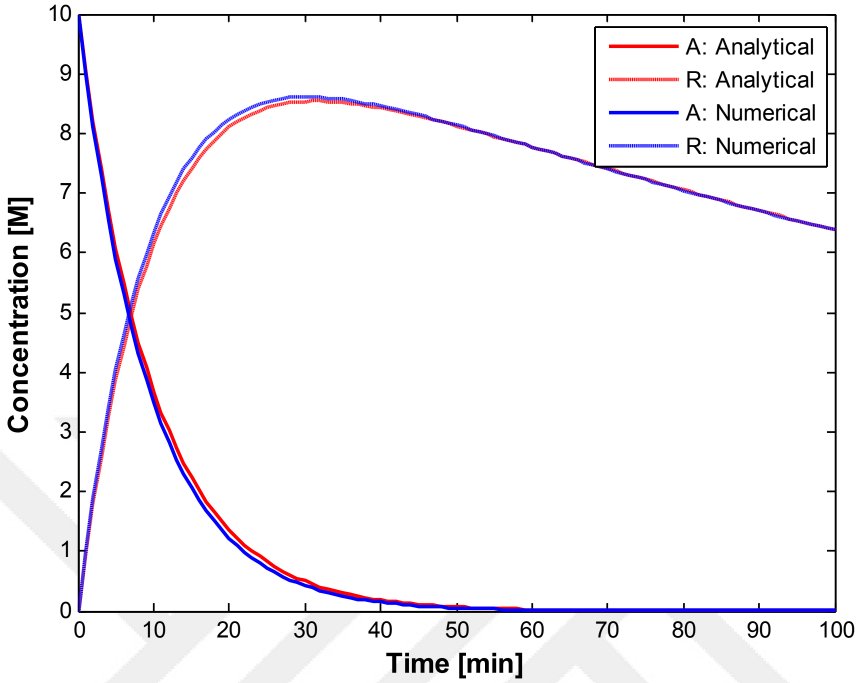


Figure A.2 Concentration profile with $k_1 = 0.1\ min^{-1}$ and $k_2 = 0.005\ min^{-1}$.

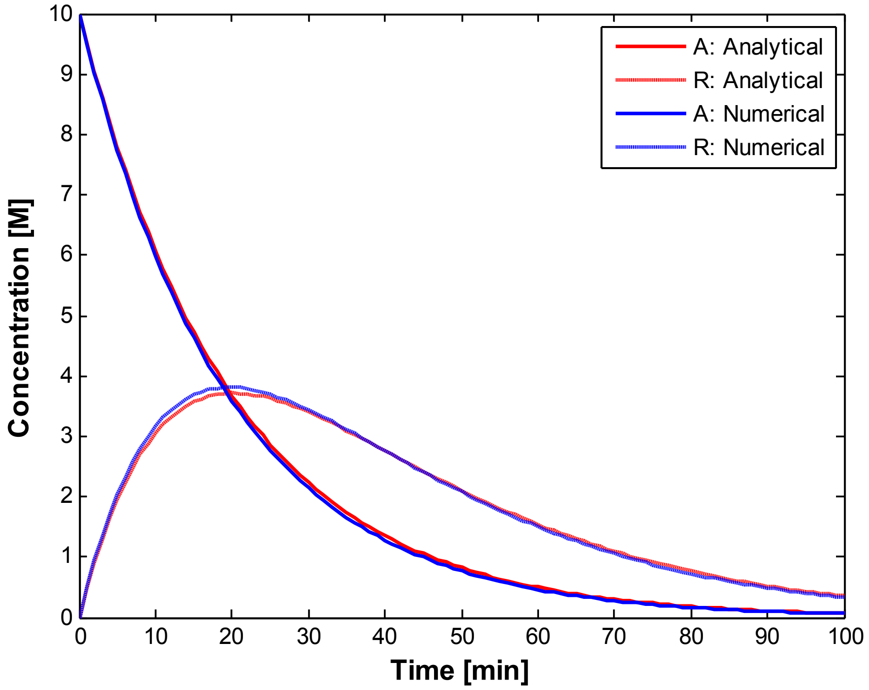


Figure A.3 Concentration profile with $k_1 = 0.05\ min^{-1}$ and $k_2 = 0.049\ min^{-1}$.

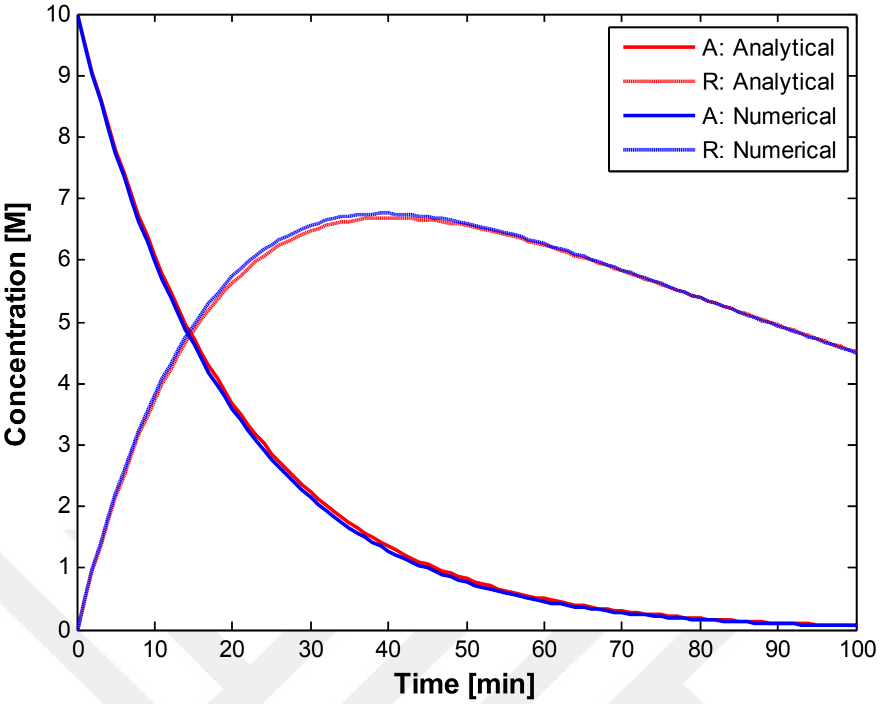


Figure A.4 Concentration profile with $k_1 = 0.05\ min^{-1}$ and $k_2 = 0.01\ min^{-1}$.

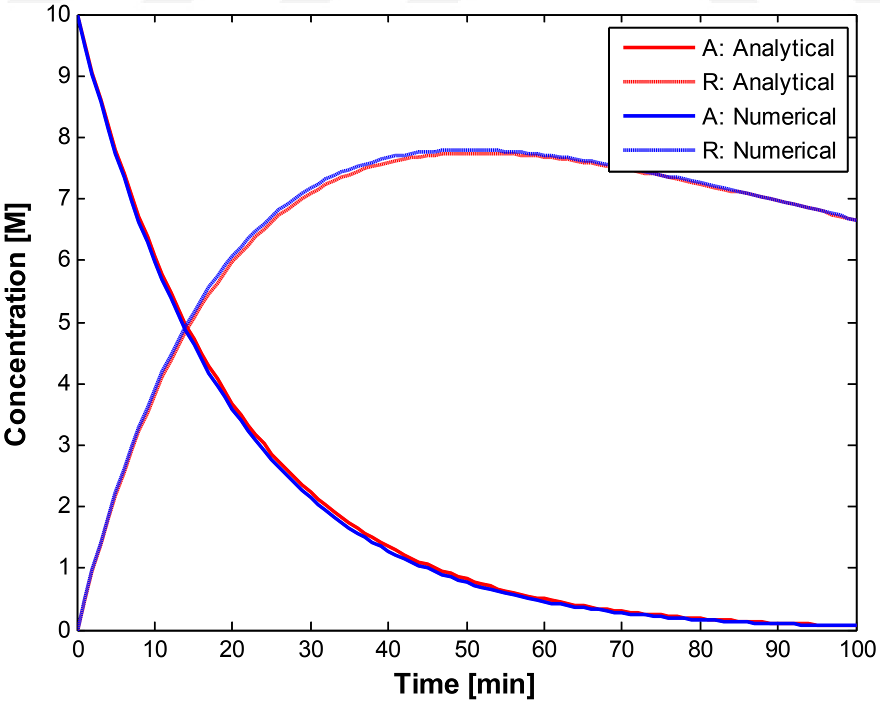


Figure A.5 Concentration profile with $k_1 = 0.05\ min^{-1}$ and $k_2 = 0.005\ min^{-1}$.

Appendix C-2: Optimal time due to various increments (Total time = 100 min)

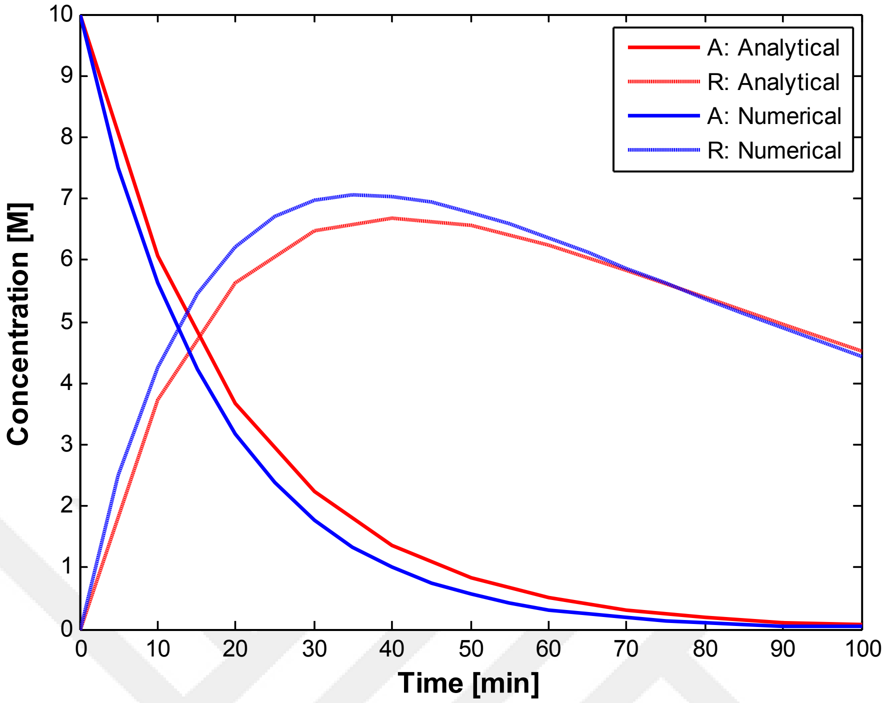


Figure A.6 Concentration profile with dt(a) = 10.0 minutes and dt(n) = 5.0 minutes

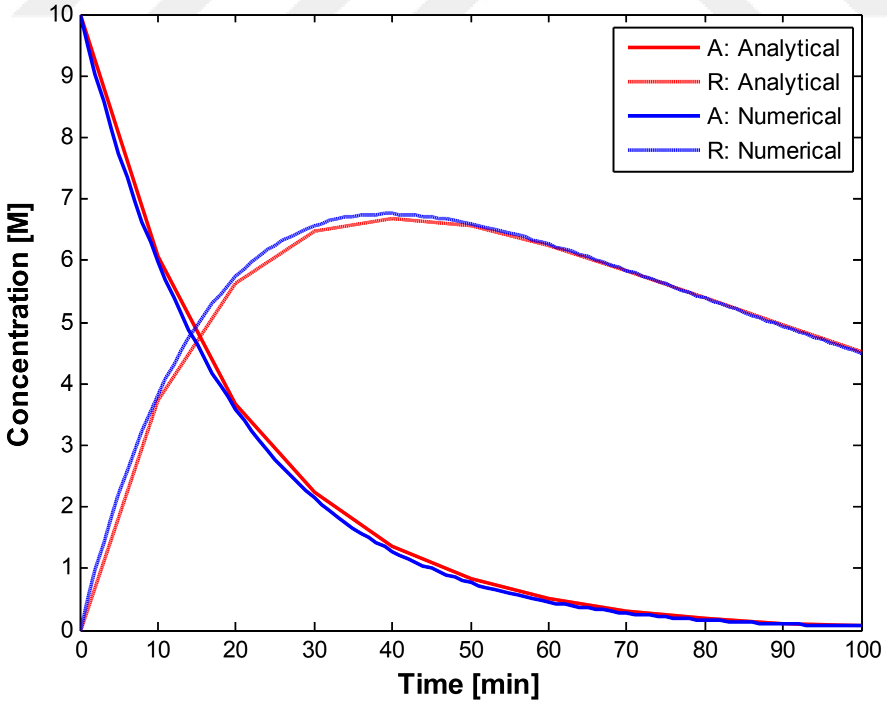


Figure A.7 Concentration profile with dt(a) = 10.0 minutes and dt(n) = 1.0 minutes

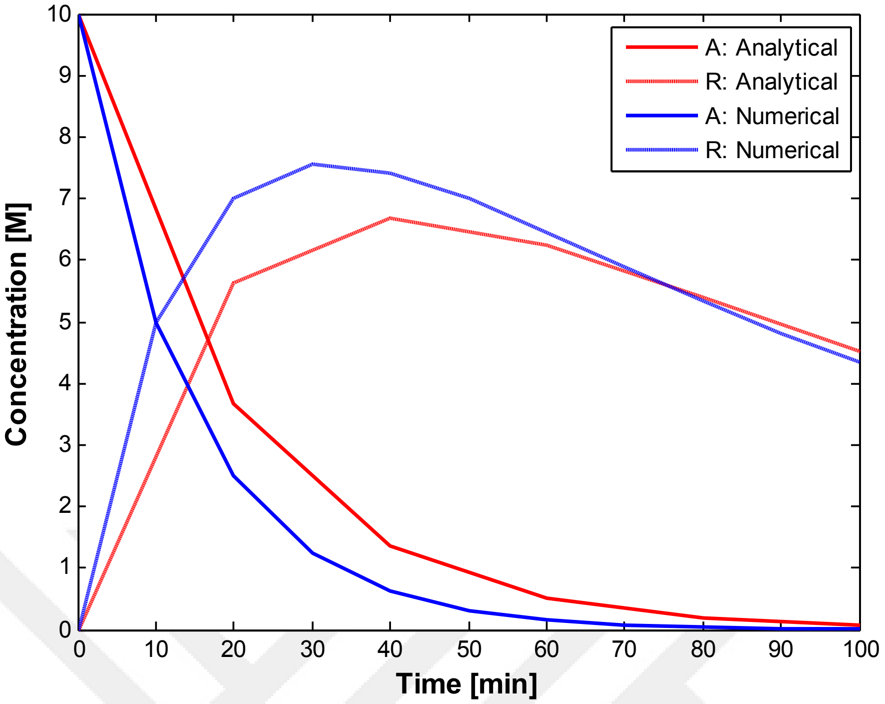


Figure A.8 Concentration profile with dt(a) = 20.0 minutes and dt(n) = 10.0 minutes

Appendix D

Equations for the non-isothermal series batch reactor (Jensen and Jeffreys, 1977)

The rate equations at any point in the reactor are expressed as the following.

$$\frac{dC_A}{dt} = -k_1 C_A = f_1$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R = f_2$$

The variation of the reaction rate constants with temperature are given below.

$$k_1 = k_{01} exp\left(-\frac{E_1}{R_{gas}T}\right) \qquad k_2 = k_{02} exp\left(-\frac{E_2}{R_{gas}T}\right)$$

It is required to maximize the yield of R. That is $C_R(\theta)$ must be a maximum. Then the objective function is arranged where θ is the optimal time.

$$I = C_R(\theta) - C_R(0) = \int_0^\theta \frac{dC_R}{dt} dt = \int_0^\theta f_2 dt$$

The adjoint functions are given below, where in this problem $f_0(C,T) = f_2$.

$$\frac{d\lambda_1}{dt} = -\frac{\delta f_0}{\delta C_A} - \sum_{j=1}^{n} \frac{\delta f_j}{\delta C_A} \lambda_j$$

Then

$\frac{\delta f_0}{\delta C_A} = k_1$ and $\frac{\delta f_1}{\delta C_A} \lambda_1 = -k_1 \lambda_1$, also $\frac{\delta f_2}{\delta C_R} \lambda_2 = k_1 \lambda_2$

and $\frac{\delta f_0}{\delta C_R} = -k_2$, $\frac{\delta f_1}{\delta C_A} \lambda_1 = 0$ and $\frac{\delta f_2}{\delta C_R} \lambda_2 = -k_2 \lambda_2$

$\frac{d\lambda_1}{dt} = k_1(\lambda_1 - \lambda_2) - k_1$ and $\frac{d\lambda_2}{dt} = k_2(\lambda_2 + 1)$

Now the temperature T must be chosen to maximize the Hamiltonian expression.

$H = f_0 + \sum_{i=1}^{n} f_i \lambda_i$ or $\frac{\delta H}{\delta T} = \frac{\delta f_0}{\delta T} + \frac{\delta}{\delta T} \sum_{i=1}^{n} f_i \lambda_i$

where

$\frac{\delta f_0}{\delta T} = C_A \frac{\delta k_1}{\delta T} - C_R \frac{\delta k_2}{\delta T}$ (at any plane in the reactor)

$$= \frac{k_{01} C_A E_1}{R_{gas} T^2} exp\left(-\frac{E_1}{R_{gas} T}\right) - \frac{k_{02} C_R E_2}{R_{gas} T^2} exp\left(-\frac{E_2}{R_{gas} T}\right)$$

$$\lambda_1 \frac{\delta f_1}{\delta T} = -\frac{k_{01} C_A E_1 \lambda_1}{R_{gas} T^2} exp\left(-\frac{E_1}{R_{gas} T}\right)$$

with a similar expression for $\lambda_2 \delta f_2/\delta T$. Therefore,

$$\frac{\delta H}{\delta T} = \frac{1}{R_{gas} T^2}\left[(1 - \lambda_1 + \lambda_2) k_{01} C_A E_1 exp\left(-\frac{E_1}{R_{gas} T}\right) - (1 + \lambda_2) k_{02} C_R E_2 exp\left(-\frac{E_2}{R_{gas} T}\right)\right]$$

The complete problem is now posed as the solution of the following equations.

$$\frac{d\lambda_1}{dt} = k_1(\lambda_1 - \lambda_2 - 1)$$

$$\frac{d\lambda_2}{dt} = k_2(\lambda_2 + 1)$$

with the boundary conditions,

at $t = 0$, $C_A = 1{\cdot}0$, $C_R = 0$ and at $t = \theta$, $\lambda_1 = 0$, $\lambda_2 = 0$

The optimum temperature profile along the reactor is that which maximizes the Hamiltonian, or satisfies

$$\frac{\delta H}{\delta T} = \frac{1}{R_{gas} T^2}[(\lambda_2 + 1 - \lambda_1) k_1 C_A E_1 - (\lambda_2 + 1) k_2 C_R E_2] = 0$$

The gradient method was selected for this step, thus

$$T_{new} = T_{old} + \alpha \frac{\delta H}{\delta T}$$

If the desired turning value in H is reached, $\delta H/\delta T$ will be zero and the optimum temperature profile will have been reached.

Curriculum Vitae

Personal Information

Surname/Name : Özveri Rana Gülizar

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Educational Background

High School : Hisar Educational Foundation Schools

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(2005 – 2009) Istanbul / Turkey

BSc Degree (1) : Marmara University

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(2009 – 2013) Istanbul / Turkey

BSc Degree (2) : Anadolu University

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(2010 – 2015) Eskişehir / Turkey

MSc Degree : Marmara University

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(2013 - 2016) Istanbul / Turkey

Project Background

BSc Project	: Marmara University	Investigation of Calcium Pyrophosphate Dihydrate Crystallization
MSc Thesis	: Marmara University	Dynamic Optimization of Batch and Semi-Batch Chemical Processes

Work History

Long Term Intern	: (2014 – 2015) Kocaeli / Turkey	Henkel Coorporation Safety, Health & Environment Dept.
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