The Semicontinous Reactor: Modeling, Simulation and Control
Part I
Modeling and Simulation

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Abstract: Conservation equations are applied to the Semicontinuous Reactor, also known as the Semibatch Reactor (SBR) for the isothermal, adiabatic and non-isothermal case, to generate the necessary differential equations for modeling and simulation. The resulting equations, expressed in terms of dimensionless normalized variables, are solved numerically for consistency testing by means of computer algebra software (Mathcad®). The model is also expressed in terms of meaningful dimensionless groups of the Damköhler and Biot type. The consistent model is then simulated for typical combinations of operating parameters in preparation for process control and stability simulation and analysis.

The SBR is typically non steady, of relatively high operating costs and low throughputs. However high conversions can be achieved and good temperature control allows for the minimizations of unwanted side reactions by means of maintaining low concentrations of one of the reactants. This reactor is extensively used in the manufacture of high value added chemicals (fine chemicals) and in reactions where a careful control is mandatory, such as in the production of high explosives. It is used in case of multiphase reactions involving gas bubbling such as the production of mono, di and tri chlorobenzene.

Part I of this article is devoted to generating a robust modeling and simulation tool for the SBR, while Part II explores its control and stable behavior.

Key words: Semicontinuous Reactor, Semibatch Reactor, SBR control, stable behavior of reactors.

1   Introduction

A Semicontinuous Reactor or also called Semibatch Reactor (SBR) is used for small scale operations, for testing new processes in process development engineering, for the manufacture of expensive products, for processes that are difficult to be converted to continuous operation and for those processes that require a tight control of operating parameters and the minimization of unwanted side reactions by means of reactant concentration manipulation. Thus, it is used to carry out reactions involving explosives and the like. It is also used when multiphase reactions are being carried out, such as the continuous bubbling of a gaseous reactant in a liquid medium.

The SBR is inherently unsteady and there are two basic types of SBR operations. In the first one, as shown in Figure 1, a reactant (A) is slowly added to a reactor containing another reactant B, loaded prior to the beginning of the reaction run. Several tactics of addition of A can be applied, as well as different set ups. The reactant A can be added continuously at a constant rate as the reaction proceeds, or fed in a varying rate sequence as a function of time. This approach is used mainly when unwanted side reactions are to be avoided, or when the reactions involved are highly exothermic. In some reactions, the reactant A is a gas that is continuously bubbled through liquid B, such as in the cases of reactions involving *ammonolysis, chlorination* and *hydrolysis*. In the second type, reactants A and B are charged simultaneously and one of the products is continuously withdrawn in order to shift equilibrium and attaining this way, higher conversions. Also higher concentrations are achieved this way, with a corresponding reduction of purifying costs, increase rate of reaction and reduced reaction times. When one of the reactants is removed from the reactor by vaporization the reaction operation is called *reactive distillation,* such as the case of *acetylation* and *esterification reactions*. One typical example of the later one is the production of *ethyl acetate* and other aromatic esters, where the reversible reaction equilibrium is shifted to the right increasing the achievable conversion by removal of a volatile byproduct. It is also the case when glycerin is continuously withdrawn in the production of bio-diesel, even though for this reaction the byproduct is not vaporized but rather removed as an insoluble dense phase.

Only the first type of SBR is considered for the present work.
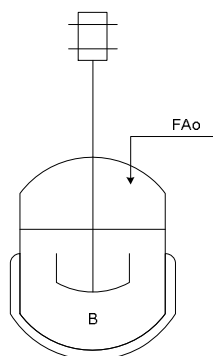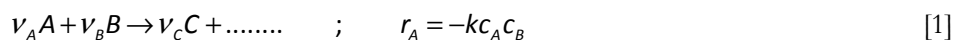
Figure 1: A Semi-continuous Chemical Reactor (SBR) of the first type. Reactant A is added to the reactor containing only B at the beginning of the run.

1 Conservation of matter applied to SBR: the mathematics.

1.1 Second order elementary reaction rate: the isothermal case.

Consider the following elementary liquid phase reaction

$$v_A A + v_B B \rightarrow v_C C + \ldots\ldots\ldots \quad ; \quad r_A = -k c_A c_B \tag{1}$$

where A is added to a vessel containing pure B, where the chemical reaction takes place. Balances performed on the number of moles of A and B, taking the system as the contents of the reactor, leads to, for A

$$\frac{dN_A}{dt} = F_{Ao} + r_A V(t) \quad ; \quad N_A(0) = 0 \tag{2}$$

N_A is the number of moles of A, F_{Ao}, the molar feed rate, V the volume of reactants and t, time. For B,

$$\frac{dN_B}{dt} = r_B V(t) \quad ; \quad \frac{dN_B}{dt} = \frac{v_B}{v_A} r_A V(t) \quad ; \quad \frac{v_A}{v_B} \frac{dN_B}{dt} = r_A V(t) \quad ; \quad N_B(0) = N_{B0}$$

$$\tag{3}$$

For the elementary chemical reaction considered, $r_A / v_A = r_B / v_B$; $r_B = r_A (v_B / v_A)$. The following equation is derived by elimination of the chemical reaction rate terms in equations [2] and [3]:

$$\frac{v_A}{v_B} \frac{dN_B}{dt} = \frac{dN_A}{dt} - F_A(t) \quad ; \quad \frac{v_A}{v_B} dN_B = dN_A - F_A(t)dt \tag{4}$$

that upon integration renders

$$\frac{V_A}{V_B}\int_{N_B=N_{B0}}^{N_B}dN_B=\int_{N_A=0}^{N_A}dN_A-\int_{t=0}^{t}F_A(t)dt \quad ; \quad N_A=-\frac{V_A}{V_B}(N_{B0}-N_B)+\int_{t=0}^{t}F_A(t)dt \quad [5]$$

This expression for the number of moles of A can be introduced in Equation [3], with the rate expression written in terms of the number of moles

$$\frac{dN_B}{dt}=-\frac{k(T)N_B(-\frac{V_A}{V_B}(N_{B0}-N_B)+\int_{t=0}^{t}F_A(t)dt)}{V(t)} \quad ; \quad N_B(0)=N_{B0} \quad [6]$$

For the simple case for which the feed rate is constant (F_A)

$$\frac{dN_B}{dt}=-\frac{k(T)N_B\left[-\frac{V_A}{V_B}(N_{B0}-N_B)+F_At\right]}{V(t)} \quad ; \quad N_B(0)=N_{B0} \quad [7]$$

The volume V is a function of time In Equation [7]. Its time dependence can be derived by a global material balance on the reactor contents, ϱ being the density of the reactor contents and ϱ_o that of the feed

$$\frac{d(V\rho)}{dt}=v_o\rho_o \quad [8]$$

If the density of the reactors content is the same as the density of the feed

$$\frac{dV}{dt}=v_o \quad ; \quad V(0)=V_o \quad [9]$$

that can be integrated to give

$$V=V_o+v_ot \quad [10]$$

By substitution in Equation [7]

$$\frac{dN_B}{dt}=-\frac{k(T)N_B\left[-\frac{V_A}{V_B}(N_{B0}-N_B)+F_At\right]}{V_o+v_ot} \quad ; \quad N_B(0)=N_{B0} \quad [11]$$

This equation has the restriction that the feed F_{Af} stops when the total number of moles of A, N_{Af}, has been added to the system. Therefore a feeding time t_f is defined by the equation

$$\int_{t=0}^{t_f}F_A(t)dt=N_{Af} \quad [12]$$

For the case of constant feed rate, the feeding time becomes

$$t_f = \frac{N_{Af}}{F_A} = \frac{N_{Af}}{\upsilon_o c_{Af}} = \frac{N_{Bo} v_A}{\upsilon_o c_{Af} v_B} \qquad \rightarrow \qquad N_{Af} = N_{Bo} \frac{v_A}{v_B} \tag{13}$$

Equation [11] can be converted to a dimensionless form using the following variables, the conversion X of B and the initial spatial time $\tau_o = V_o/\upsilon_o$

$$X = \frac{N_{Bo} - N_B}{N_{Bo}} = 1 - \frac{N_B}{N_{Bo}} \quad ; \quad \theta = \frac{v_B c_{Af} \upsilon_o t}{v_A c_{Bo} V_o} \quad ; \quad \theta = \frac{v_B c_{Af} t}{v_A c_{Bo} \tau_o} \quad ; \quad \tau_o = \frac{V_o}{\upsilon_o} \tag{14}$$

to give the following equation

$$\frac{dX}{d\theta} = K(T) \frac{(1-X)(\theta - X)}{(1+\varepsilon\theta)} \quad ; \quad X(0) = 0 \tag{15}$$

where $\varepsilon = v_A c_{Bo}/v_B c_{Af} = \upsilon_0 t_f / V\big|_{t=t_f}$ the ratio of the stoichiometric initial concentrations of B in the reactor and A in the feed. The K(T) term is $K(T) = k(T) N_{Bo} v_A / v_B \upsilon_o$, that can be expressed in in a more convenient form

$$K(T) = \frac{k(T) N_{Bo} v_A}{v_B \upsilon_o} = k(T) \frac{N_{Bo} v_A c_{Af}}{v_B \upsilon_o c_{Af}} = k(T) t_f c_{Af} \tag{16}$$

From Equation [14], for a dimensionless final feed time corresponding to θ = 1,

$$t_f = \frac{v_A c_{Bo}}{v_B c_{Af}} \tau_o = \varepsilon \tau_o \tag{17}$$

Therefore, Equation [16] becomes

$$K(T) = \varepsilon \tau_o c_{Af} k(T) \tag{18}$$

And the final equation for the SBR up to the final feed time is

$$\frac{dX}{d\theta} = \varepsilon \tau_o c_{Af} k(T) \frac{(1-X)(\theta - X)}{(1+\varepsilon\theta)} \quad ; \quad X(0) = 0 \tag{19}$$

For the cases where a stoichiometric amount of A is added to the reaction mixture, the reaction proceeds as if it were taking place in a batch reactor after the addition of the reactant A is terminated, that occurs when θ = 1. Thus, for θ > 1, the equation reduces to

$$\frac{dX}{d\theta} = \varepsilon \tau_o c_{Af} k(T) \frac{(1-X)^2}{(1+\varepsilon)} \quad ; \quad X(1) = X\big|_{\theta=1} \tag{20}$$

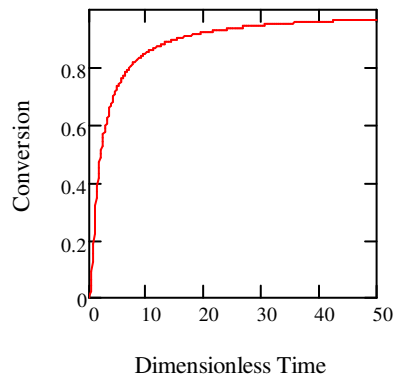This equation was solved numerically using Mathcad 15® as shown in Subprogram 1.

Figure 2: Numerical solution of Equation [19]. Fractional conversion X plotted against dimensionless time θ. The parameters used were: $\epsilon = 1$, $\tau_o = 10$ min, $c_{Ao} = 1$ mole/ft3, $c_{Bo} = 1$ mole/ft3 $n_{Bo} = 30$ moles, $n_{Ao} = 30$ moles, $k = 0.1204$ ft3/mol min.
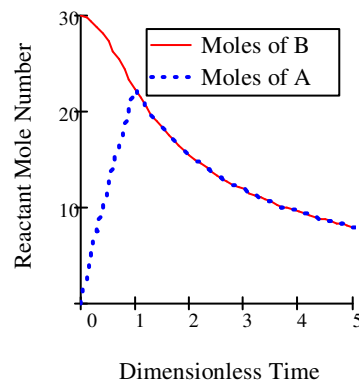

Figure 3: Numerical solution of Equation [19]. The dependence of the number of moles of B and A of time θ are displayed. The parameters used were: $\epsilon = 1$, $\tau_o = 10$ min, $c_{Ao} = 1$ mole/ft3, $c_{Bo} = 1$ mole/ft3 $n_{Bo} = 30$ moles, $n_{Ao} = 30$ moles, $k = 0.1204$ ft3/mole min.
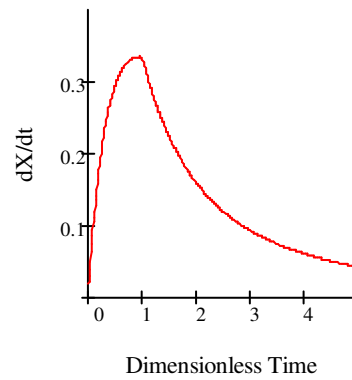
Dimensionless Time

Figure 4: Numerical solution of Equation [19]. The slope of the fractional conversion X as a function of time θ is displayed. The parameters used were: $\epsilon = 1$, $\tau_o = 10$ min, $c_{Ao} = 1$ mole/ft3, $c_{Bo} = 1$ mole/ft3 $n_{Bo} = 30$ moles, $n_{Ao} = 30$ moles, $k = 0.1204$ ft3/mole min. A discontinuity at the end of feeding period is clearly visible.
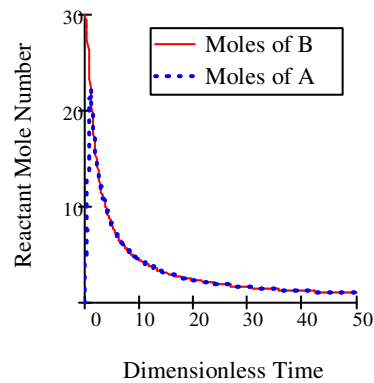

Dimensionless Time

Figure 5: Numerical solution of Equation [19]. The number of moles of B and A as a function of time θ are displayed. The parameters used were the same as those in Figure 1, but the time has been extended to 50.

$$k = 0.1204$$

$$\varepsilon := 1$$

$$\tau_o := 10$$

$$cao := 1$$

$$nbo := 30$$

$$fao := 30$$

$$FBR(\theta, X, k, \varepsilon, \tau o, cao) := \varepsilon \bullet \tau o \bullet cao \bullet k \bullet \left[\frac{(1-X)^2}{(1+\varepsilon)} \right]$$

$$FSBR(\theta, X, k, \varepsilon, \tau o, cao) := \varepsilon \bullet \tau o \bullet cao \bullet k \bullet \left[(1-X) \bullet \frac{(\theta-X)}{(1+\varepsilon \bullet \theta)} \right]$$

$$SBR(\theta, X, k, \varepsilon, \tau o, cao, FSBR, FBR) := \begin{vmatrix} FSBR(\theta, X, k, \varepsilon, \tau o, cao) & \text{if } \theta \geq 0 \wedge \theta \leq 1 \\ FBR(\theta, X, k, \varepsilon, \tau o, cao) & \text{otherwise} \end{vmatrix}$$

Given

$$\frac{d}{d\theta}X(\theta) = SBR(\theta, X(\theta), k, \varepsilon, \tau o, cao, FSBR, FBR)$$

$$X(0) = 0$$

$$\frac{d}{d\theta}nb(\theta) = -nbo \bullet \frac{d}{d\theta}X(\theta)$$

$$nb(0) = nbo$$

$$\frac{d}{d\theta}na(\theta) = fao \bullet \Phi(1-\theta) - nbo \bullet \frac{d}{d\theta}X(\theta)$$

$$na(0) = 0$$

$$\begin{pmatrix} Xx \\ Nb \\ Na \end{pmatrix} := Odesolve\left[\begin{pmatrix} X \\ nb \\ na \end{pmatrix}, \theta, 50 \right]$$

Figure 6: Subprogram 1. Numerical solution of equations [19] and [20]. A logical function has been employed to take into account the end of feeding at time $\theta = 1$, as well as the Heaviside step function Φ.

2 Second order elementary reaction rate: the adiabatic case.

For this case an adiabatic energy balance is required

$$\begin{bmatrix} \text{Rate of Energy} \\ \text{Accumulation} \end{bmatrix} = \begin{bmatrix} \text{Rate of Energy} \\ \text{In} \end{bmatrix} \qquad [21]$$

or

$$\frac{d}{dt}\left[n_T U_m \right] = H_{m,f} F_f \qquad [22]$$

Where n_T refers to the total number of moles, U_m, the molar internal energy, $H_{m,f}$ the molar enthalpy of the feed stream and F_f, the molar feed rate. If species A, B, C, D and S (solvent) are the chemical species in the reactor, then

$$\frac{d}{dt}\Big[n_A U_{m,A} + n_B U_{m,B} + n_C U_{m,C} + n_D U_{m,D} + n_S U_{m,S}\Big] = F_f c_f (T_f - T_{ref}) \qquad [23]$$

Here c_f is the molar specific heat capacity of the feed, T_f the feed temperature and T_{ref} a reference temperature. Expanding Equation [22] and neglecting the internal energy of mixing

$$n_A \frac{dU_{m,A}}{dt} + n_B \frac{dU_{m,B}}{dt} + n_C \frac{dU_{m,C}}{dt} + n_D \frac{dU_{m,D}}{dt} + U_{m,A} \frac{dn_A}{dt} + U_{m,B} \frac{dn_B}{dt} + U_{m,C} \frac{dn_C}{dt} +$$
$$+ U_{m,D} \frac{dn_D}{dt} + \frac{d}{dt}\Big[n_S U_{m,S}\Big] = F_f c_f (T_f - T_{ref})$$
$$[24]$$

If it is assumed that $-\nu_A = -\nu_B = \nu_C = \nu_D = 1$, applying the extent of reaction definition

$$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \frac{dn_C}{dt} = \frac{dn_D}{dt} \qquad [25]$$

that upon substitution and rearranging in Equation [24] becomes

$$n_A \frac{dU_{m,A}}{dt} + n_B \frac{dU_{m,B}}{dt} + n_C \frac{dU_{m,C}}{dt} + n_D \frac{dU_{m,D}}{dt} + \Big[U_{m,A} + U_{m,B} - U_{m,C} - U_{m,D}\Big]\frac{dn_B}{dt} +$$
$$n_S \frac{dU_{m,S}}{dt} + U_{m,S} \frac{dn_S}{dt} = F_f c_f (T_f - T_{ref})$$
$$[26]$$

where n_s stands for the number of moles of solvent

$$\Big[n_A c_A + n_B c_B + n_C c_C + n_D c_D + n_S c_S\Big]\frac{dT}{dt} - \Delta_r U_m \frac{dn_B}{dt} + U_{m,S}\frac{dn_S}{dt} = F_f c_f (T_f - T_{ref}) \qquad [27]$$

since, by definition

$$-\Big[U_{m,A} + U_{m,B} - U_{m,C} - U_{m,D}\Big] = \Delta_r U_m \qquad [28]$$

A mass balance on the solvent s gives, c_{sf} being the molar concentration of solvent in the feed

$$\frac{dn_S}{dt} = F_f c_{Sf} \quad ; \quad \frac{dn_S}{dt} = F_{Af}\frac{c_{Sf}}{c_{Af}} \quad ; \quad n_S = n_{So} + F_f c_{Sf} t \quad ; \quad n_S = n_{So} + F_{Af}\frac{c_{Sf}}{c_{Af}}t$$
$$[29]$$

where n_{so} is the initial number of moles of solvent in the reactor. By substitution in Equation [27]

$$\left[n_A c_A + n_B c_B + n_C c_C + n_D c_D + \left(n_{So} + F_f c_{Sf} t\right) c_S\right]\frac{dT}{dt} - \Delta_r U_m \frac{dn_B}{dt} + U_{m,S} F_{Af} \frac{c_{Sf}}{c_{Af}}$$
$$= F_f c_f (T_f - T_{ref})$$

[30]

The total number of moles of reactants and solvent present in the reactor at the beginning g of the run, n_{to}, are

$$n_{Ao} + n_{Bo} + n_{Co} + n_{Do} + n_{So} = n_{to}$$

[31]

Since the density and the heat capacity can be considered constant due to the relative low concentration of reactants, then the initial heat capacity of the reactor contents is

$$n_A c_{p,A} + n_B c_{p,B} + n_C c_{p,C} + n_D c_{p,D} + n_{So} c_{p,S} = C_o$$

[32]

If the feed of reactant A and the solvent associated with it is taken into account, then a heat capacity of the reactors content, C(t) can be derived, taking into account that the number of moles is constant due to the stoichiometry of the reaction, except for the addition of reactant A and the accompanying solvent

$$C(t) = C_o + F_{Af} t c_f$$

[33]

Since $F_f t c_f$ is the heat capacity of the feed. Then Equation [29] becomes, accepting also that for a diluted liquid reaction $U_m \approx H_m$

$$U_{m,S} \frac{dn_S}{dt} = c_f (T_f - T_{ref}) F_{Af} \frac{c_{Sf}}{c_{Af}}$$

[34]

Therefore

$$\left[C_o + F_f t c_f\right]\frac{dT}{dt} - \Delta_r H_m \frac{dn_B}{dt} = \left[F_f - F_{Af} \frac{c_{Sf}}{c_{Af}}\right] c_f (T_f - T_{ref})$$

[35]

And also, assuming that the average specific heat capacity of the feed is about the same as that of A

$$F_f - F_{Af} \frac{c_{Sf}}{c_{Af}} = F_{Af}$$

[36]

Therefore equation [30] becomes

$$\frac{dT}{dt} = \frac{F_A c_f (T_f - T_{ref}) + \Delta_r H_m \dfrac{dn_B}{dt}}{\left[C_o + F_f t c_f\right]}$$

[37]

The denominator of this equation is simply the heat capacity of the reactor contents, $C = C(t)$

$$\frac{dT}{dt} = \frac{F_A c_f (T_f - T_{ref}) + \Delta_r H_m \frac{dn_B}{dt}}{C(t)} \quad ; \quad T(0) = T_o \qquad [38]$$

and for the BR

$$\frac{dT}{dt} = \frac{1}{C(t_f)} \left[\Delta_r H_m \frac{dn_B}{dt} \right] \qquad [39]$$

If the reactant feed is fed at the reference temperature, the equations become for the SBR and BR reactors

$$\frac{dT}{dt} = \frac{\Delta_r H_m \frac{dn_B}{dt}}{C(t)} \quad ; \quad T(0) = T_o \quad ; \quad \frac{dT}{dt} = \frac{1}{C(t_f)} \left[\Delta_r H_m \frac{dn_B}{dt} \right] \quad ; \quad T(0) = T_o$$

$$[40]$$

That can be expressed in dimensionless form by means of the following variables, where T_s refers to the set point (the desired temperature for the reaction to be carried out at) and T_{ref}, a reference temperature, say 298 K)

$$\theta = \frac{v_B c_{Af} t}{v_A c_{Bo} \tau_o} \quad ; \quad \tau = \frac{T - T_{ref}}{T_s - T_{ref}} \quad ; \quad X = \frac{n_{Bo} - n_B}{n_{Bo}} \qquad [41]$$

and

$$dt = \frac{v_A c_{Bo} \tau_o}{v_B c_{Af}} d\theta \quad ; \quad dT = (T_s - T_{ref}) d\tau \quad ; \quad \frac{dn_B}{d\theta} = -n_{Bo} \frac{dX}{d\theta} \qquad [42]$$

to give

$$\frac{d\tau}{d\theta} = \frac{1}{\left[C(\theta)(T_s - T_{ref}) \right]} \left[\Gamma_A c_f (T_f - T_{ref}) - \Delta_r H_m n_{Bo} \frac{dX}{d\theta} \right] \quad ; \quad \tau(0) = 1 \qquad [43]$$

where Γ_A is the A reactant feed in terms of the dimensional time defined before. For the BR case, after the feed period elapses

$$\frac{d\tau}{d\theta} = -\frac{\Delta_r H_m n_{Bo} \frac{dX}{d\theta}}{C(1)(T_s - T_{ref})} \quad ; \quad \tau(1) = \tau \Big|_{\theta_{SBR} = 1} \qquad [44]$$

The equations for the SBR-BR reactors become

$$\frac{d\tau}{d\theta} = -\frac{\Delta_r H_m n_{Bo} \frac{dX}{d\theta}}{C(\theta)\left(T_s - T_{ref}\right)} \quad ; \quad \tau(0) = 1 \quad ; \quad \frac{d\tau}{d\theta} = -\frac{\Delta_r H_m n_{Bo} \frac{dX}{d\theta}}{C(1)\left(T_s - T_{ref}\right)} \quad ; \quad \tau(1) = \tau\Big|_{\theta_{SBR}=1}$$

[45]

where

$$C(\theta) = C_o + \Gamma_A c_f \theta$$

[46]

In this equation, the term Γ_A is the feed rate of reactant A in moles of A for the dimensionless time (the feed ends at $\theta = 1$. For the BR reactor, the term $\Delta_r H_m n_{Bo} / C(1)\left(T_s - T_{ref}\right)$ is a Damköhler type dimensionless group (Da) that represents the ratio of heat generated by chemical reaction when the total number of moles of B reacts over the heat capacity of the reactor's content when the feed has been concluded, referred to the set point temperature. Thus

$$\frac{d\tau}{d\theta} = \frac{Da Da_f}{\left[Da_f - Da\left(1-\theta\right)\right]} \frac{dX}{d\theta} \quad ; \quad \tau(0) = 1 \quad ; \quad \frac{d\tau}{d\theta} = Da\frac{dX}{d\theta} \quad ; \quad \tau(1) = \tau\Big|_{\theta_{SBR}=1}$$

[47]

Here the Damköhler type dimensionless groups are, (including the Damköhler group referred to the feed Da_f)

$$Da = \frac{-\Delta_r H_m n_{Bo}}{C(1)\left(T_s - T_{ref}\right)} \quad ; \quad Da_f = \frac{-\Delta_r H_m n_{Bo}}{\Gamma_A c_f\left(T_s - T_{ref}\right)}$$

[48]

The set of resulting differential equations [19], [20], [37] and [38] I solved using Mathcad 15, as shown in Subprogram 2.
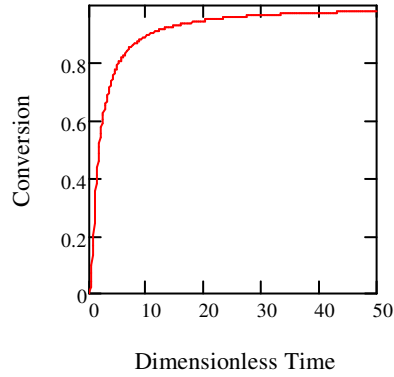
Figure 7: Numerical solution of Equation [19]. Fractional conversion X plotted against dimensionless time θ. The parameters used were: $\epsilon = 1$, $\tau_o = 10$ min, $c_{Ao} = 1$ mole/ft3, $c_{Bo} = 1$ mole/ft3 $n_{Bo} = 30$ moles, $n_{Ao} = 30$ moles, $k = 0.1204$ ft3/mol min.
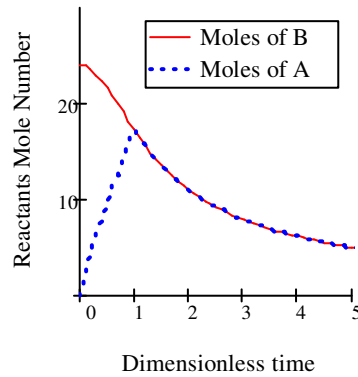

Figure 8: Numerical solution for the adiabatic case. The number of moles of B and A are displayed as function of time θ. The parameters used were the same as above.
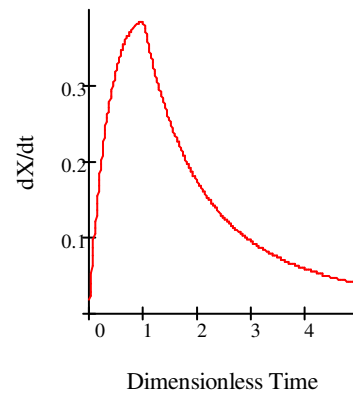
Figure 9: Numerical solution for the adiabatic case. Slope of the fractional conversion X as a function of time θ. The parameters used were the same as above. A discontinuity at the end of feeding period is clearly visible.
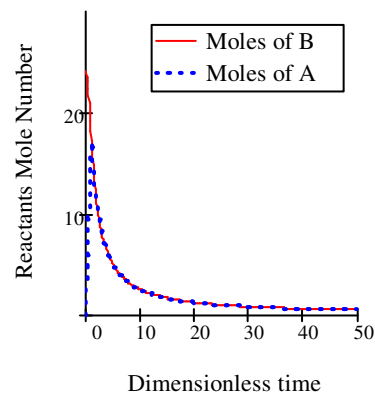

Figure 10: Numerical solution for the adiabatic case. Slope of the fractional conversion X as a function of time θ. The parameters used were the same as above.
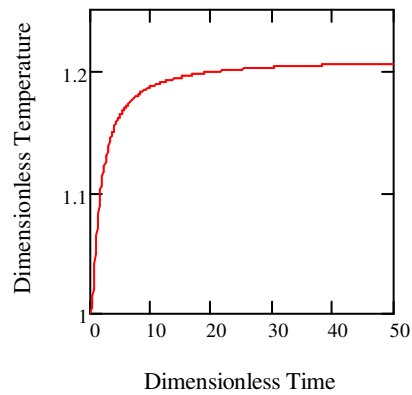
Figure 11: Numerical solution for the adiabatic case. The dimensionless temperature as a function of the dimensionless time is displayed. The parameters used were the same as above. A steady state temperature is reached.
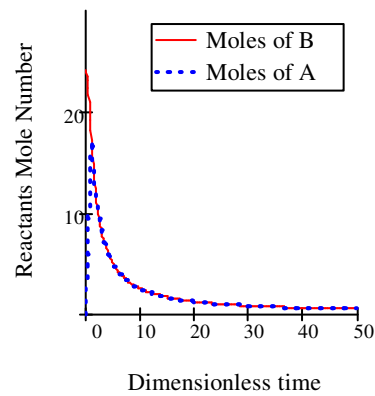
Figure 12: Numerical solution for the adiabatic case. The number of moles of A and B as functions of time are displayed. The parameters used were the same as above. A steady state temperature is reached.

Figure 13: Adiabatic case numerical solution for the SBR. The dimensionless temperature as a function of the dimensionless time is displayed. The parameters used were the same as above. A steady state temperature is reached.
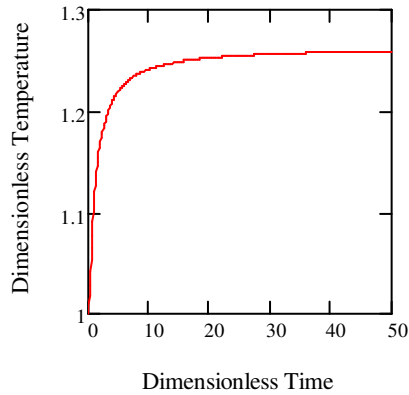
$\varepsilon := 1 \qquad \tau o := 10 \qquad cao := 1 \qquad ts := 343 \qquad tref := 298 \qquad nso := 456 \qquad cf := 300 \qquad nbo := 24$

$fao := 24$

$\Delta rH := -10.8 \bullet 10^4 \qquad Faf := 24$

$Ka(T, ts, tref) := 2.58 \bullet 10^5 \bullet \exp\left[\dfrac{-5000}{T \bullet (ts - tref) + tref}\right]$

$FSBRA(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) := \varepsilon \bullet \tau o \bullet cao \bullet Ka(T, ts, tref) \bullet \left[(1 - X) \bullet \dfrac{(\theta - X)}{(1 + \varepsilon \bullet \theta)}\right]$

$SBRA(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, FSBRA, FBRA, Ka) := \begin{vmatrix} FSBRA(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) & \text{if } \theta \geq 0 \wedge \theta \leq 1 \\ FBRA(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) & \text{otherwise} \end{vmatrix}$

$FBRA(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) := \varepsilon \bullet \tau o \bullet cao \bullet Ka(T, ts, tref) \bullet \left[\dfrac{(1 - X)^2}{(1 + \varepsilon)}\right]$

$CC(\theta, nso, Faf) := \begin{vmatrix} cc \leftarrow (nso + 19 \bullet Faf \bullet \theta) \bullet 300 & \text{if } \theta \geq 0 \wedge \theta \leq 1 \\ cc \leftarrow (nso + 19 \bullet Faf) \bullet 300 & \text{otherwise} \\ cc \end{vmatrix}$

$RESBRB(\theta, Da, Daf, DX) := \begin{vmatrix} f \leftarrow \dfrac{Da \bullet Daf}{Daf - Da \bullet (1 - \theta)} DX & \text{if } \theta \geq 0 \wedge \theta \leq 1 \\ f \leftarrow Da \bullet DX & \text{otherwise} \end{vmatrix}$

$Da := \dfrac{-\Delta rH \bullet nbo}{CC(1, nso, Faf) \bullet (ts - tref)} = 0.2105$

$Daf := \dfrac{-\Delta rH \bullet nbo}{Faf \bullet cf \bullet (ts - tref)} = 8.0000$

$$\frac{d}{d\theta}X(\theta) = SBRA(\theta, X(\theta), T(\theta), \varepsilon, \tau_o, cao, ts, tref, FSBRA, FBRA, Ka)$$

$$\frac{d}{d\theta}T(\theta) = RESBRB\left(\theta, Da, Daf, \frac{d}{d\theta}X(\theta)\right)$$

$$\frac{d}{d\theta}nb(\theta) = -nbo \bullet \frac{d}{d\theta}X(\theta)$$

$$\frac{d}{d\theta}na(\theta) = Faf \bullet \Phi(1 - \theta) - nbo \bullet \frac{d}{d\theta}X(\theta)$$

$$na(0) = 0$$

$$\begin{pmatrix} Xx \\ Tc \\ Nb \\ Na \end{pmatrix} := Odesolve\left[\begin{pmatrix} X \\ T \\ nb \\ na \end{pmatrix}, \theta, 50\right]$$
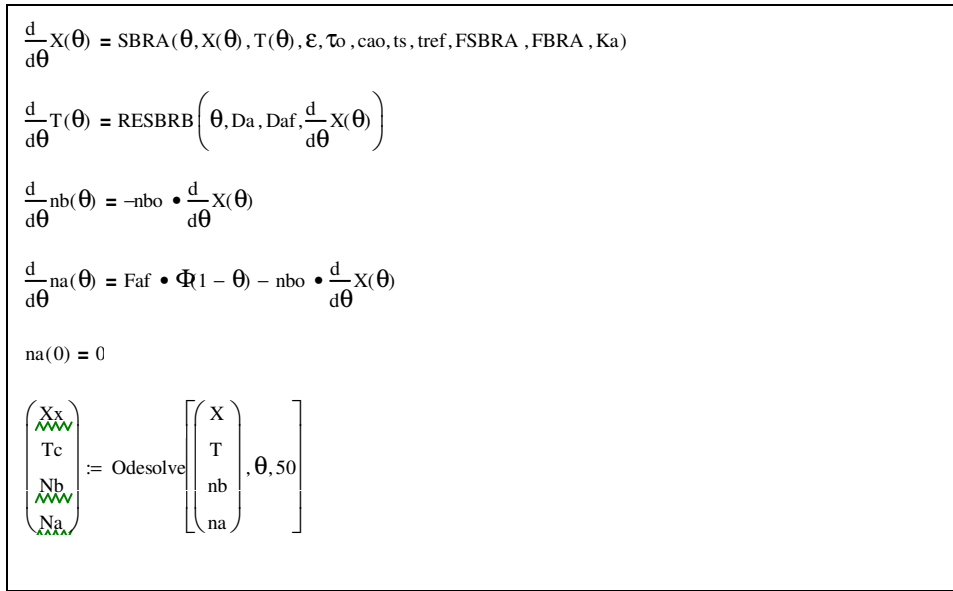
Figure 14: **Subprogram 2.** Numerical solution of the adiabatic case (equations [19], [20], [37] and [38]) using Mathcad.

3   Second order elementary reaction rate: the non adiabatic case

For this case the mass balance is, of course, the same as before. The energy balance of Equation [38] becomes

$$\frac{dT}{dt} = \frac{F_A c_f (T_f - T_{ref}) + \Delta_r H_m \dfrac{dn_B}{dt} - UA(t)(T - T_w)}{\left[C_o + F_f t \, c_f\right]} \tag{49}$$

where the cooling effect of the water jacket has been added, the heat transfer area A being a function of time. In terms of the dimensionless variables defined before. Tw is the temperature of the cooling jacket water Thus Equation [49] becomes

$$\frac{d\tau}{d\theta} = \frac{\dfrac{\nu_A c_{Bo} \tau_o}{\nu_B c_{Af}}}{C(\theta)\left(T_s - T_{ref}\right)}\left[\Gamma_A c_f (T_f - T_{ref}) - \frac{\Delta_r H_m n_{Bo}}{\dfrac{\nu_A c_{Bo} \tau_o}{\nu_B c_{Af}}}\frac{dX}{d\theta} - UA(\theta)(T_s - T_{ref})\left[\tau - \tau_w\right]\right] \quad ; \quad \tau(0) = 1 \tag{50}$$

Here the dimensionless temperature τ_w of the cooling media is

$$\tau_w = \frac{T_w - T_{ref}}{T_s - T_{ref}} \tag{51}$$

Setting the feed temperature T_f equal to the reference temperature T_{ref}

$$\frac{d\tau}{d\theta} = \frac{\dfrac{\nu_A c_{Bo} T_o}{\nu_B c_{Af}}}{C(\theta)\left(T_s - T_{ref}\right)} \left[\frac{-\Delta_r H_m n_{Bo}}{\dfrac{\nu_A c_{Bo} T_o}{\nu_B c_{Af}}} \frac{dX}{d\theta} - UA(\theta)(T_s - T_{ref})\left[\tau - \tau_w\right] \right] \quad ; \quad \tau(0) = 1 \tag{52}$$

Since the density of the reacting media is supposed constant, as is the specific heat capacity, then the heat transfer area $A(t)$ is proportional to the number of moles of the reactor contents at any time

$$n_t(t) = n_{So} + n_{Bo} + F_f t \qquad ; \qquad n_t(\theta) = n_{So} + n_{Bo} + \Gamma_f \theta \tag{53}$$

and therefore

$$A(\theta) = A_o \frac{n_t(\theta))}{n_t(0)} = A_o \left[1 + \frac{\Gamma_f}{n_{So} + n_{Bo}} \theta\right] \tag{54}$$

Rearranging Equation [52]

$$\frac{d\tau}{d\theta} = \frac{U \dfrac{\nu_A c_{Bo} T_o}{\nu_B c_{Af}} A(\theta)}{C(\theta)} \left[\frac{-\Delta_r H_m n_{Bo}}{U \dfrac{\nu_A c_{Bo} T_o}{\nu_B c_{Af}} A(\theta)(T_s - T_{ref})} \frac{dX}{d\theta} - \left[\tau - \tau_w\right] \right] \quad ; \quad \tau(0) = 1 \tag{55}$$

and

$$\frac{d\tau}{d\theta} = \frac{U \dfrac{\nu_A c_{Bo} T_o}{\nu_B c_{Af}} A_o \left[\dfrac{1 + \dfrac{\Gamma_f}{n_{So} + n_{Bo}}\theta}{1 + \dfrac{\Gamma_A c_f \theta}{C_o}}\right]}{C_o} \left[\frac{-\Delta_r H_m n_{Bo}}{U \dfrac{\nu_A c_{Bo} T_o}{\nu_B c_{Af}} A_o (T_s - T_{ref})\left[1 + \dfrac{\Gamma_f}{n_{So} + n_{Bo}}\theta\right]} \frac{dX}{d\theta} - \left[\tau - \tau_w\right] \right] \tag{56}$$

There are some meaningful dimensionless groups in this equation

$$Da_r = \frac{-\Delta_r H_m n_{Bo}}{U\dfrac{\nu_A c_{Bo}\tau_o}{\nu_B c_{Af}}A_o(T_s - T_{ref})} \quad ; \quad D_1 = \frac{U\dfrac{\nu_A c_{Bo}\tau_o}{\nu_B c_{Af}}A_o}{C_o} \quad ; \quad D_2 = \frac{\Gamma_f}{n_{So} + n_{Bo}} \quad ; \quad D_3 = \frac{\Gamma_A c_f}{C_o}$$

$$[57]$$

Here the Da_r group, another Damköhler type dimensionless group related to the chemical reaction is the ratio of the total heat generated by it when the total number of moles B have been consumed to the initial heat transfer rate; D_1, the heat transfer per unit temperature difference taking into account the initial area available for heat transfer over the initial heat capacity; D_2 the ratio of the molar feed over the initial number of moles of reactants and D3 the ratio of the heat capacity of the feed of reactant A over the initial contents heat capacity of the reactor.

Upon substitution of Equation [57] on Equation [56] for the SBR up to $\theta = 1$

$$\frac{d\tau}{d\theta} = D_1\left[\frac{1 + D_2\theta}{1 + D_3\theta}\right]\left[\frac{Da_r}{[1 + D_2\theta]}\frac{dX}{d\theta} - (\tau - \tau_w)\right] \quad ; \quad \tau(0) = 1 \qquad [58]$$

And for the BR behavior ($\theta > 1$)

$$\frac{d\tau}{d\theta} = D_1\left[\frac{1 + D_2}{1 + D_3}\right]\left[\frac{Da_r}{[1 + D_2]}\frac{dX}{d\theta} - (\tau - \tau_w)\right] \quad ; \quad \tau(1) = \tau\big|_{\theta_{SBR}=1} \qquad [59]$$

Now it is necessary to derive another equation for T_w from an energy balance on the cooling jacket.

$$\frac{dT_w}{dt} = \frac{UA(t)(T - T_w) - F_w c_w(T_w - T_{ref})}{C_w} \quad ; \quad T_w(0) = T_{ref} \qquad [60]$$

Here T_w is the temperature, F_w the flow rate, c_w the specific heat and C_w the heat capacity of the coolant. The cooling jacket is represented by a uniform temperature bath with equal inlet and outlet flow rates. In terms of the dimensionless variables defined before

$$\frac{d\tau_w}{d\theta} = \frac{U\dfrac{\nu_A c_{Bo}\tau_o}{\nu_B c_{Af}}A(\theta)\big[\tau - \tau_w\big] - F_w \dfrac{\nu_A c_{Bo}\tau_o}{\nu_B c_{Af}}c_w\tau_w}{C_w} \quad ; \quad \tau_w(0) = 0 \qquad [61]$$

or

$$\frac{d\tau_w}{d\theta} = \frac{\dfrac{\nu_A c_{Bo} \tau_o}{\nu_B c_{Af}} UA_o}{C_w}\left[1 + \frac{\Gamma_f}{n_{So} + n_{Bo}}\theta\right]\left[\tau - \tau_w\right] - \frac{\dfrac{\nu_A c_{Bo} \tau_o}{\nu_B c_{Af}} F_w c_w}{C_w}\tau_w \quad ; \quad \tau_w(0) = 0$$

[62]

Here again there are some Damköhler type dimensionless groups, namely

$$D_4 = \frac{\dfrac{\nu_A c_{Bo} \tau_o}{\nu_B c_{Af}} UA_o}{C_w} \quad ; \quad D_2 = \frac{\Gamma_f}{n_{So} + n_{Bo}} \quad ; \quad D_5 = \frac{\dfrac{\nu_A c_{Bo} \tau_o}{\nu_B c_{Af}} F_w c_w}{C_w}$$

[63]

D_4 is the heat transfer per unit temperature difference taking into account the initial area available for heat transfer over the heat capacity of the coolant jacket and its contents; D_2 the ratio of the molar feed over the initial number of moles of reactants and D_5 the ratio of the heat capacity of the feed of reactant A over the heat capacity of the coolant jacket and its contents. Hence

$$\frac{d\tau_w}{d\theta} = D_4\left[1 + D_2\theta\right]\left[\tau - \tau_w\right] - D_5\tau_w \quad ; \quad \tau_w(0) = 0$$

[64]

Equations [47], [58] and [64] constitute the non-adiabatic second order type one SBR reactor model. The numeric solution obtained using Mathcad is depicted in Subprogram 3, while the data has been plotted in the figures shown below.
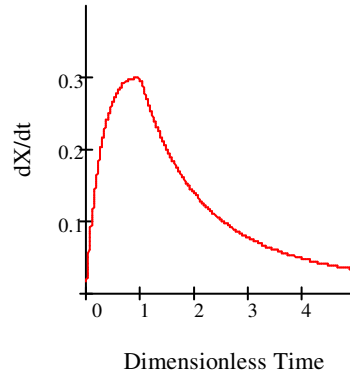

Figure 15: Numerical solution for the non-adiabatic case. Slope of the fractional conversion X as a function of time θ. The parameters used are depicted in Subprogram 3 below. A discontinuity at the end of the feeding period is clearly visible as before.
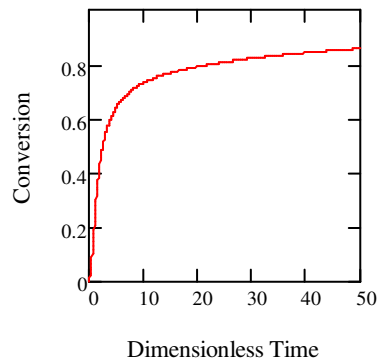
Figure 16: Fractional conversion X plotted against dimensionless time θ. The parameters used are depicted in Subprogram 3.
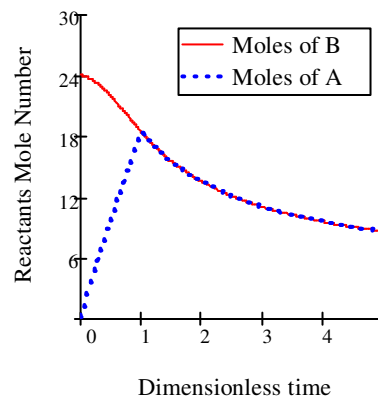

Figure 17: Numerical Solution for the SBR for the non-adiabatic case. The number of moles of B and A are displayed as functions of time θ. The parameters used were the same as above.
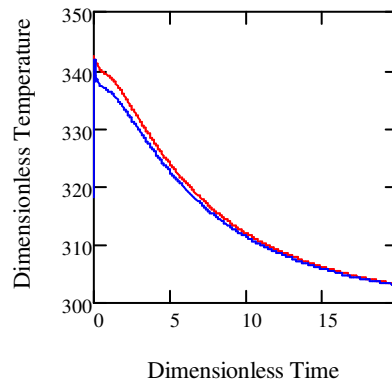
Figure 18: Non–adiabatic case numerical solution for the SBR. The parameters used were the same as above. The upper line refers to the reactants temperature, while the lower one, the cooling water temperature.
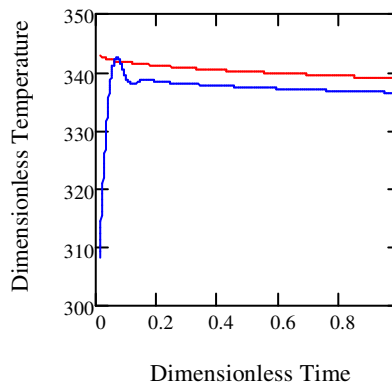

Figure 19: Non–adiabatic case numerical solution for the SBR. The parameters used were the same as above. The upper line refers to the reactants temperature, while the lower one, the cooling water temperature.

$\varepsilon := 1 \qquad cao := 1 \qquad ts := 343 \qquad tref := 298 \qquad nso := 456 \qquad cf := 300 \qquad Co := 300 \bullet nso \qquad nbo := 24$

$fao := 24 \qquad \tau o := 10 \qquad \Delta rH := -10.8 \bullet 10^4 \qquad Faf := 24 \qquad UAo := 40000 \qquad Cw := 2000 \qquad F := 24$

$cw := 500 \qquad Fw := \dfrac{100}{18} = 5.5556$

$Ka(T, ts, tref) := 2.58 \bullet 10^5 \bullet \exp\left[\dfrac{-5000}{T \bullet (ts - tref) + tref}\right]$

$$\text{FSBRA}(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) := \varepsilon \bullet \tau o \bullet cao \bullet Ka(T, ts, tref) \bullet \left[(1 - X) \bullet \frac{(\theta - X)}{(1 + \varepsilon \bullet \theta)} \right]$$

$$\text{FBRA}(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) := \varepsilon \bullet \tau o \bullet cao \bullet Ka(T, ts, tref) \bullet \left[\frac{(1 - X)^2}{(1 + \varepsilon)} \right]$$

$$\text{SBRA}(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, FSBRA, FBRA, Ka) := \begin{vmatrix} \text{FSBRA}(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) & \text{if } \theta \geq 0 \wedge \theta \leq 1 \\ \text{FBRA}(\theta, X, T, \varepsilon, \tau o, cao, ts, tref, Ka) & \text{otherwise} \end{vmatrix}$$

$$\text{CC}(\theta, nso, Faf) := \begin{vmatrix} cc \leftarrow (nso + 19 \bullet Faf \bullet \theta) \bullet 300 & \text{if } \theta \geq 0 \wedge \theta \leq 1 \\ cc \leftarrow (nso + 19 \bullet Faf) \bullet 300 & \text{otherwise} \\ cc \end{vmatrix}$$

$$\text{TSBR}(\theta, t, tw, Dar, D1, D2, D3, DX) := \begin{vmatrix} f \leftarrow D1 \bullet \left(\frac{1 + D2 \bullet \theta}{1 + D3 \bullet \theta} \right) \bullet \left[\left(\frac{Dar}{1 + D2 \bullet \theta} \right) \bullet DX - (t - tw) \right] & \text{if } \theta \geq 0 \wedge \theta \leq 1 \\ f \leftarrow D1 \bullet \left(\frac{1 + D2}{1 + D3} \right) \bullet \left[\left(\frac{Dar}{1 + D2} \right) \bullet DX - (t - tw) \right] & \text{otherwise} \end{vmatrix}$$

$$\text{TWSBR}(\theta, t, tw, D2, D4, D5, DX) := D4 \bullet (1 + D2 \bullet \theta) \bullet (t - tw) - D5 \bullet tw$$

$$\text{Dar} := \frac{-\Delta rH \bullet nbo}{UAo \bullet \tau o \bullet (ts - tref)} = 0.1440 \qquad \text{D1} := \frac{UAo \bullet \tau o}{Co} = 2.9240 \qquad \text{D2} := \frac{F}{nso + nbo} = 0.0500$$

$$\text{D3} := \frac{Faf \bullet cf}{Co} = 0.0526$$

$$\text{D4} := \frac{UAo \bullet \tau o}{Cw} = 200.0000 \qquad \text{D5} := \frac{Fw \bullet \tau o \bullet cw}{Cw} = 13.8889$$

Given

$$\frac{d}{d\theta} X(\theta) = \text{SBRA}(\theta, X(\theta), T(\theta), \varepsilon, \tau o, cao, ts, tref, FSBRA, FBRA, Ka) \qquad X(0) = 0$$

$$\frac{d}{d\theta} T(\theta) = \text{TSBR}\left(\theta, T(\theta), Tw(\theta), Dar, D1, D2, D3, \frac{d}{d\theta} X(\theta) \right) \qquad T(0) = 1$$

$$\frac{d}{d\theta} Tw(\theta) = \text{TWSBR}\left(\theta, T(\theta), Tw(\theta), D2, D4, D5, \frac{d}{d\theta} X(\theta) \right) \qquad Tw(0) = 0$$

$$\frac{d}{d\theta} nb(\theta) = -nbo \bullet \frac{d}{d\theta} X(\theta) \qquad nb(0) = nbo$$

$$\frac{d}{d\theta} na(\theta) = Faf \bullet \Phi(1 - \theta) - nbo \bullet \frac{d}{d\theta} X(\theta) \qquad na(0) = 0$$

$$\begin{pmatrix} Xx \\ Tc \\ Twc \\ Nb \\ Na \end{pmatrix} := \text{Odesolve}\left[\begin{pmatrix} X \\ T \\ Tw \\ nb \\ na \end{pmatrix}, \theta, 50 \right]$$

Figure 20: Numerical solution for the non-adiabatic case using Mathcad. The parameters considered are depicted in the program.

4   Conclusions

A versatile macroscopic model for the SBR reactor has been derived for the isothermal, adiabatic and non-adiabatic cases. A second order elementary reaction was studied. Other kinetics can be studied using the same approach. The model is well suited for its solution utilizing digital computers and modern computer algebra software. The non-adiabatic case is especially interesting since it can be used for modeling nonlinear process control, an area of great interest that is precisely the subject for the next part of this article.

Notation

Variables

A, B, C, D = chemical species A, B, C, D respectively. A refers also to the area available for heat transfer.

c = specific heat capacity

C = Heat capacity of the reactor contents

F = reactant feed rate

H = Enthalpy

n, N = number of moles

k = chemical reaction rate constant

r = chemical reaction rate

t = time

T = Temperature

U = Internal energy, also the global heat transfer coefficient

V = volume of the chemical reaction media

z = factor de compresión

Parameters

Da, Da_f = dimensionless Damköhler type parameters defined by Equation [48]

Da_r = another Damköhler type parameter defined by Equation [57]

D_1, D_2, D_3 = parameters for the energy balance defined by Equation [57]

Greek Letters

Δ = incremental operator, when referred to chemical reactions gives the enthalpy or internal energy of reaction

ϱ = density of the chemical reaction medium

ε = ratio of the stoichiometric initial concentrations of species B in the reactor and A in the feed

Γ = Feed rate of reactant

ν = stoichiometric coefficient of an elementary chemical reaction.

$\square$ = volumetric feed rate

X = chemical reaction conversion

Θ = dimensionless time

τ = space time, also a dimensionless temperature

Subscripts

A, B, C, D = species A, B, C, D respectively

o, 0 = refers to a parameter at the beginning of the run

f = refers to a parameter at the end of the run and also to the feed

m = molar, specific property

ref = reference, used with T refers to a reference temperature

S = refers to the solvent

w = refers to the cooling medium