**BatchReactor Application Example**

**Food Industry**

**Simulation of Batch Starch Enzymatic Hydrolysis With User Defined Kinetics**

**Example Purpose**

The main interest of this example is to show how user can very simply describe his own kinetic models using the advanced mode available in Simulis Reactions, the chemical reactions server used in BatchReactor software. This food processing example deals with the enzymatic hydrolysis of starch to form fermentable carbohydrates (glucose, maltose and maltotriose) in beer production. The mathematical modeling of the reaction mechanisms (Arrhenius law with enzyme activity terms) uses specific equations which are not available in standard chemical reaction libraries such as Simulis Reactions.

**Access**

- ✔ Free-Internet
- □ Restricted to ProSim clients
- □ Restricted
- □ Confidential

**Corresponding BatchReactor Files**

- BATCHREA_EX_EN - Beer Run E1.pbpr
- BATCHREA_EX_EN - Beer Run E7.pbpr
- BATCHREA_EX_EN - Beer Run E10.pbpr

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Reader is reminded that this use case is only an example and should not be used for other purposes. Although this example is based on actual case it may not be considered as typical nor are the data used always the most accurate available. ProSim shall have no responsibility or liability for damages arising out of or related to the use of the results of calculations based on this example.
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1. INTRODUCTION

This example is taken from [BRA03] and involves the enzymatic hydrolysis of starch during the mashing stage of beer production. Starch is used as an energy store by many plants. They store glucose in the form of starch as it is osmotically inactive and can be stored much more compactly [WIK15].

Through the process of mashing, starch molecules are broken to form dextrin and fermentable carbohydrates like glucose, maltose and maltotriose. In a slower rate, dextrin molecules are also broken to form the same products. The responsible enzymes for these reactions are α and β amylases. While α-amylase acts in the formation of all the carbohydrates cited, β-amylase acts only in the maltose formation. Before the hydrolysis, the starch must pass through a gelatinization stage by the increase of temperature, as the enzymes affect only the gelatinized form of the starch. The big and small grains of starch have different behaviors during this stage. It is thus necessary to use different kinetic expressions for each case.

In the model used in this work the kinetics of the hydrolysis reactions are related to the enzymatic activities of α and β amylases, which depend on the operating temperature. This influence is represented by polynomial laws that can change depending on the temperature range. The denaturation of the enzymes active sites also requires attention, as it influences the enzymes activities directly. It is thus necessary to take all of this into account when implementing this model in BatchReactor.
2. REACTION MECHANISM

The mechanisms of the reactions taken into account are the following ones.

✓ Big grains of non gelatinized starch forming gelatinized starch:

\[
\text{Big grains of non gelatinized starch} \xrightarrow{\text{Temperature}} \text{Gelatinized starch}
\]  

(R1)

✓ Small grains of non gelatinized starch forming gelatinized starch:

\[
\text{Small grains of non gelatinized starch} \xrightarrow{\text{Temperature}} \text{Gelatinized starch}
\]  

(R2)

✓ Gelatinized starch forming glucose:

\[
\text{Gelatinized starch} + n \text{ water} \xrightarrow{\alpha-\text{amylase}} n \text{ Glucose}
\]

For example,

\[
(C_6H_{10}O_5)_n + n H_2O \xrightarrow{\alpha-\text{amylase}} n C_6H_{12}O_6 
\]  

(R3)

✓ Gelatinized starch forming maltose:

\[
\text{Gelatinized starch} + \frac{n}{2} \text{ Water} \xrightarrow{\alpha/\beta-\text{amylase}} \frac{n}{2} \text{ Maltose}
\]

For example,

\[
(C_6H_{10}O_5)_n + \frac{n}{2} H_2O \xrightarrow{\alpha/\beta-\text{amylase}} \frac{n}{2} C_{12}H_{22}O_{11} 
\]  

(R4)

✓ Gelatinized starch forming maltotriose:

\[
\text{Gelatinized starch} + \frac{n}{3} \text{ Water} \xrightarrow{\alpha-\text{amylase}} \frac{n}{3} \text{ Maltotriose}
\]

For example,

\[
(C_6H_{10}O_5)_n + \frac{n}{3} H_2O \xrightarrow{\alpha-\text{amylase}} \frac{n}{3} C_{18}H_{32}O_{16} 
\]  

(R5)

✓ Gelatinized starch forming dextrin:

\[
\text{Gelatinized starch} \xrightarrow{\alpha-\text{amylase}} x \text{ Dextrin}
\]

For example,

\[
(C_6H_{10}O_5)_n \xrightarrow{\alpha-\text{amylase}} x (C_6H_{10}O_5)_{n/x} 
\]  

(R6)
✓ Dextrin forming glucose:

\[ \text{Dextrin} + \frac{n}{x} \text{Water} \xrightarrow{\alpha-amyrase} \frac{n}{x} \text{Glucose} \]

For example,

\[ (C_6H_{10}O_5)_{n/x} + \frac{n}{x} H_2O \xrightarrow{\alpha-amyrase} \frac{n}{x} C_6H_{12}O_6 \] (R7)

✓ Dextrin forming maltose:

\[ \text{Dextrin} + \frac{n}{2x} \text{Water} \xrightarrow{\alpha/\beta-amyrase} \frac{n}{2x} \text{Maltose} \]

For example,

\[ (C_6H_{10}O_5)_{n/x} + \frac{n}{2x} H_2O \xrightarrow{\alpha/\beta-amyrase} \frac{n}{2x} C_{12}H_{22}O_{11} \] (R8)

✓ Dextrin forming maltotriose:

\[ \text{Dextrin} + \frac{n}{3x} \text{Water} \xrightarrow{\alpha-amyrase} \frac{n}{3x} \text{Maltotriose} \]

For example,

\[ (C_6H_{10}O_5)_{n/x} + \frac{n}{3x} H_2O \xrightarrow{\alpha-amyrase} \frac{n}{3x} C_{18}H_{32}O_{16} \] (R9)

The values for \( n \) and \( x \) can be freely chosen by the user because they do not influence the results when the system is treated with mass concentrations. For the purpose of this work the values \( n = 12000 \) and \( x = 1000 \) were chosen, as these values satisfy the mass balance.
All of these reactions can be represented by the following diagram.

For the denaturation of the enzymes active sites, the following equations are considered.

- **Active α sites forming inactive α sites:**
  
  \[
  \text{One active } \alpha \text{ site} \rightarrow \text{One inactive } \alpha \text{ site}
  \]  
  \hspace{1cm} (R10)

- **Active β sites forming inactive β sites**
  
  \[
  \text{One active } \beta \text{ site} \rightarrow \text{One inactive } \beta \text{ site}
  \]  
  \hspace{1cm} (R11)
3. COMPONENTS

Components which are taken into account in the simulation are:

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (*)</td>
<td>7732-18-5</td>
</tr>
<tr>
<td>Glucose (*)</td>
<td>50-99-7</td>
</tr>
<tr>
<td>Maltose (*)</td>
<td>57-50-1</td>
</tr>
<tr>
<td>Maltotriose</td>
<td></td>
</tr>
<tr>
<td>Dextrin</td>
<td></td>
</tr>
<tr>
<td>Small grains of non gelatinized starch</td>
<td></td>
</tr>
<tr>
<td>Big grains of non gelatinized starch</td>
<td></td>
</tr>
<tr>
<td>Gelatinized starch</td>
<td></td>
</tr>
<tr>
<td>Active $\alpha$ site</td>
<td></td>
</tr>
<tr>
<td>Inactive $\alpha$ site</td>
<td></td>
</tr>
<tr>
<td>Active $\beta$ site</td>
<td></td>
</tr>
<tr>
<td>Inactive $\beta$ site</td>
<td></td>
</tr>
<tr>
<td>Malt</td>
<td></td>
</tr>
</tbody>
</table>

Compounds with an asterisk are taken from the standard database of Simulis Thermodynamics, thermodynamics server used in BatchReactor. The thermophysical properties stored in this database are the DIPPR recommended values [ROW2015]. The malt compound was added to represent the system’s dry mass, as all of the experimental data is based on the dry mass quantity.

Maltotriose, dextrin and the three types of starch are obtained by cloning glucose and changing the:

- Specific name
- CAS number (arbitrary numbers)
- Molecular weight
- Liquid density (same value as water)

The other compounds (active and inactive $\alpha$ site, active and inactive $\beta$ site and malt) were created by the function “Add a new compound” of Simulis Thermodynamics. For the active and inactive sites it is arbitrarily adopted a molecular weight of 10 000 g/mol. For the malt, it is adopted the starch’s molecular weight (malt has a composition of 50-60 wt. % of starch). The other used properties are:

- CAS number : Arbitrary number
- Enthalpy of formation for ideal gas at 25°C : 0 J/mol
- Vapor and liquid mass specific heat : Same as water
- Vapor pressure : Parameters chosen to avoid the vaporization
  \[ \ln(P^0) = -30 \]  (Equation 101)
- Vaporization enthalpy : 0 J/mol
- Liquid density : Same as water

For all compounds the liquid density is assumed to be equal to the density of water.
4. THERMODYNAMIC MODEL

Most of the components are non-polar and non-volatile in the reaction conditions. Reactions occurred at atmospheric pressure and at temperatures between 37 °C and 76°C. The liquid phase was thus assimilated to an ideal solution and gas phase was assumed to follow the perfect gas law. The “ideal” profile of Simulis Thermodynamics is then chosen.

5. REACTION MATHEMATICAL MODEL

The transformation of starch into fermentable carbohydrates and dextrin is represented by stoichiometric reactions. The kinetics of these reactions is related to the activities of α and β amylases enzymes. The model equations are taken from [BRA03].

- Rate of big grains of starch gelatinization:

\[
\begin{align*}
    r_g &= k_{g1} \times \exp \left( \frac{-E_{g1}}{RT} \right) [S_3] \quad \text{for } T < 60^\circ C \\
    r_g &= k_{g2} \times \exp \left( \frac{-E_{g2}}{RT} \right) [S_3] \quad \text{for } T > 60^\circ C
\end{align*}
\]  \tag{R1}

- Rate of small grains of starch gelatinization:

\[
\begin{align*}
    r_{sg} &= 0 \quad \text{for } T < 60^\circ C \\
    r_{sg} &= k_{sg} \times \exp \left( \frac{-E_{sg}}{RT} \right) [S_{ss}] \quad \text{for } T > 60^\circ C
\end{align*}
\]  \tag{R2}

The temperature of 60°C is the threshold temperature \( T_g \). According to [BRA03], it is assumed that the gelatinization of small grains occurs only above this temperature.

- Rate of gelatinized starch forming glucose:

\[
    r_{gl} = k_{gl} \times a_\alpha \times [S_g] \quad \tag{R3}
\]

- Rate of gelatinized starch forming maltose:

\[
    r_{mal} = k_{a,mal} \times a_\alpha \times [S_g] + k_{\beta,mal} \times a_\beta \times [S_g] \quad \tag{R4}
\]

- Rate of gelatinized starch forming maltotriose:

\[
    r_{mit} = k_{mit} \times a_\alpha \times [S_g] \quad \tag{R5}
\]
Rate of gelatinized starch forming dextrin:
\[ r_{\text{dex}} = k_{\text{dex}} \times a_\alpha \times [S_g] \]  \hspace{1cm} (R6)

Rate of dextrin forming glucose:
\[ r'_{gl} = k'_{gl} \times a_\alpha \times [D] \]  \hspace{1cm} (R7)

Rate of dextrin forming maltose:
\[ r'_{mal} = k'_{a,mal} \times a_\alpha \times [D] + k'_{\beta,mal} \times a_\beta \times [D] \]  \hspace{1cm} (R8)

Rate of dextrin forming maltotriose:
\[ r'_{mit} = k'_{m,mit} \times a_\alpha \times [D] \]  \hspace{1cm} (R9)

Rate of denaturation of active sites:
\[ r_{da} = k_{da} \times \exp\left(\frac{-E_{da}}{RT}\right)[E_\alpha] \]  \hspace{1cm} (R10)
\[ r_{db} = k_{db} \times \exp\left(\frac{-E_{db}}{RT}\right)[E_\beta] \]  \hspace{1cm} (R11)

Enzyme activities \(a_\alpha\) and \(a_\beta\):
\[ a_\alpha = [E_\alpha] \times a_5(T) \]
\[ a_\beta = [E_\beta] \times a_5(T) \]

The relative specific enzyme activity \(a_5(T)\) is represented by polynomial equations that change according to the temperature range, as shown in the figure of the next page.
Polynomials for the relation between temperature and the relative specific activity for $\alpha$- and $\beta$-amylases

All parameters taken from [BRA03] are presented in the following table. For the purpose of this work it is considered that 1 U = 1 g, as U (units) is an abstract concept.

<table>
<thead>
<tr>
<th>$k_{gl}$</th>
<th>$k_{\alpha, mal}$</th>
<th>$k_{\beta, mal}$</th>
<th>$k_{mrt}$</th>
<th>$k_{dex}$</th>
<th>$k'_{gl}$</th>
<th>$k'_{\alpha, mal}$</th>
<th>$k'_{\beta, mal}$</th>
<th>$k'_{mrt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(kg/(U.s))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.023</td>
<td>0.389</td>
<td>0.137</td>
<td>0.117</td>
<td>0.317</td>
<td>2.9e^-8</td>
<td>1.2e^-7</td>
<td>8.4e^-8</td>
<td>1.5e^-8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$k_{g1}$</th>
<th>$k_{g2}$</th>
<th>$k_{sg}$</th>
<th>$k_{d\alpha}$</th>
<th>$k_{d\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s^-1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.7e^31</td>
<td>3.1e^14</td>
<td>4.18e^45</td>
<td>6.9e^30</td>
<td>7.6e^60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E_{g1}$</th>
<th>$E_{g2}$</th>
<th>$E_{sg}$</th>
<th>$E_{d\alpha}$</th>
<th>$E_{d\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>220 600</td>
<td>108 300</td>
<td>253 600</td>
<td>224 200</td>
<td>410 700</td>
</tr>
</tbody>
</table>
6. REACTION MODEL IMPLEMENTATION USING SIMULIS REACTIONS

The reactions presented in the paragraphs 2 and 5 were described in Simulis Reactions, as shown in the next screenshot.

The two reactions of denaturation of active sites follow “classic” Arrhenius laws. Thus, they are described with the standard Simulis Reactions interface. Regarding the other reactions, user “interpreted” kinetic rate model was used to implement mathematical models presented by [BRA03] as shown on the next screenshot. Thanks to this functionality of Simulis Reactions, user can write his own code for kinetic model using VBScript (Microsoft Visual Basic Scripting Edition), which is an interpreted language (i.e. it doesn't require compilation before being executed). For more information about VBScript language, user can refer to:

http://msdn.microsoft.com/en-us/library/10aew7h6(v=vs.84).aspx

http://en.wikipedia.org/wiki/VBScript

All reactions take place in the liquid phase.

The heat of reaction of each reaction is assumed to be 0.
The VBS code for the (R1) reaction is the following one:

```
'CHECK PROCEDURE
Function CheckRate
    CheckRate = True
End Function

'REACTION RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
    'Model parameters
    R  = 8.31  '/(mol.s)
    Tg = 333.15 'K) , Tg = 60°C
    If (T < Tg) Then
        kg = 5.7E31 '/(s-1)
        Eg = 220600 '/(J/mol)
    ElseIf (T >= Tg) Then
        kg = 3.1E14 '/(s-1)
        Eg = 108300 '/(J/mol)
    End If
    'Calculation of the molar volume
    Vml = ThermoCalculator.PCalcVml(T,P,z)
    'Units conversion
    'Molar volume
```
Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
Set Quantity = Repository.QuantityByName("Molar volume")
Vml = Quantity.Convert(Vml,"cm3/mol","l/mol")
'Molar mass
Set MwQty = Repository.QuantityByName("Molar mass")
'Calculation of the concentrations
CASN_BigNonGelatStarch = "55531-00-5"
For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
        If (.CasRegistryNumber = CASN_BigNonGelatStarch) Then
            ipos_BigNonGelatStarch = i-1
            Mw_BigNonGelatStarch = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            C_BigNonGelatStarch = z(ipos_BigNonGelatStarch) * Mw_BigNonGelatStarch / Vml
            Ss = C_BigNonGelatStarch 'Ss (g/l)
        End If
    End With
Next
'Calculation of the reaction rate
CalcR = kg * exp(-Eg/(R*T)) * Ss 'Reaction rate for starch production (g non gelatinized starch/l s)
CalcR = CalcR / Mw_BigNonGelatStarch 'Reaction rate for starch production (mol non gelatinized starch/l s)
End Function

'CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/L/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/L/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/L/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/L/s
'Err: Variant - Error code
Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)
    'Reaction rate
    Rate = CalcR(T, P, z)
    'Temperature derivative
dT = 0.1
    T1 = T + dT
    Rate1 = CalcR(T1, P, z)
    dRatedT = (Rate1-Rate)/dT
    'Pressure derivative
dP = 0.1
    P1 = P + dP
    Rate1 = CalcR(T, P1, z)
dRatedP = (Rate1-Rate)/dP

'Compositions derivatives
NC = ThermoCalculator.Componds.Count
Dim z1()
ReDim z1(NC-1)
For i=0 To NC-1
    For j=0 To NC-1
        z1(j) = z(j)
    Next
    dz = z1(i)*5e-6
    If (dz < 1e-8) Then
        dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j=0 To NC-1
        Tot = Tot + z1(j)
    Next
    For j=0 To NC-1
        z1(j) = z1(j) / Tot
    Next
    Rate1 = CalcR(T, P, z1)
    dRatedN(i) = (Rate1-Rate)/dz
Next
End Sub

The VBS code for the (R2) reaction is the following one:

'CHECK PROCEDURE
Function CheckRate
    CheckRate = True
End Function

'REACTION RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
    'Model parameters
    ksg = 4.18E35 '(/s-1)
    Esg = 253600 '(J/mol)
    R = 8.31 '(/mol.s)
    'Calculation of the molar volume
    Vml = ThermoCalculator.PCalcVml(T,P,z)
    'Units conversion
    'Molar volume
    Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
Set Quantity = Repository.QuantityByName("Molar volume")
Vml = Quantity.Convert(Vml,"cm3/mol","l/mol")

'Molar mass
Set MwQty = Repository.QuantityByName("Molar mass")

'Calculation of the concentrations
CASN_LittleNonGelatStarch = "55820-02-5"
For i=1 To ThermoCalculator.Compounds.Count
  With ThermoCalculator.Compounds.Items(i-1)
    If (.CasRegistryNumber = CASN_LittleNonGelatStarch) Then
      ipos_LittleNonGelatStarch = i-1
      Mw_LittleNonGelatStarch = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
      C_LittleNonGelatStarch = z(ipos_LittleNonGelatStarch) * Mw_LittleNonGelatStarch / Vml
      Sss = C_LittleNonGelatStarch
    End If
  End With
  Next

'Calculation of the reaction rate
Tg = 333.15 '(K), Tg = 60°C
If (T <= Tg) Then
  CalcR = 0 'It is considered that this reaction occurs only for temperatures > Tg
ElseIf (T > Tg) Then
  CalcR = ksg * exp(-Esg/(R*T)) * Sss
  'Reaction rate for starch production (g non gelatinized starch/l s)
  CalcR = CalcR / Mw_LittleNonGelatStarch
  'Reaction rate for starch production (mol non gelatinized starch/l s)
End If
End Function

'CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/L/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/L/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/L/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/L/s
'Err: Variant - Error code
Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)
  'Reaction rate
  Rate = CalcR(T, P, z)
  'Temperature derivative
  dT = 0.1
  T1 = T + dT
  Rate1 = CalcR(T1, P, z)
  dRatedT = (Rate1-Rate)/dT
'Pressure derivative

dP = 0.1
P1 = P + dP
Rate1 = CalcR(T, P1, z)
dRatedP = (Rate1-Rate)/dP

'Compositions derivatives

NC = ThermoCalculator.Componds.Count

Dim z1()

ReDim z1(NC-1)

For i=0 To NC-1
    For j=0 To NC-1
        z1(j) = z(j)
    Next
    dz = z1(i)*5e-6
    If (dz < 1e-8) Then
        dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j=0 To NC-1
        Tot = Tot + z1(j)
    Next
    For j=0 To NC-1
        z1(j) = z1(j) / Tot
    Next
    Rate1 = CalcR(T, P, z1)
    dRatedN(i) = (Rate1-Rate)/dz
Next
End Sub
The VBS code for the (R3) reaction is the following one:

```vbs
' CHECK PROCEDURE
Function CheckRate
    CheckRate = True
End Function

'REACTION RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
    'Model parameters
    kgl  = 0.023  ' (kg/U.s)
    R    = 8.31   ' (J/mol.K)
    Tlim = 336   ' (K), temperature that separates the two polynomials of the specific activity

    'Calculation of the specific activity
    If (T < Tlim) Then
        As_alpha = -0.00112295*T^3 + 1.091*T^2 - 352.8982*T + 38008.3367
    ElseIf (T >= Tlim) Then
        As_alpha = -0.02729377*T^2 + 17.935*T - 2937.2174
    End If

    If (As_alpha < 0) Then
        As_alpha = 0 'The specific activity cannot be negative
    End If

    'Calculation of the molar volume
    Vml = ThermoCalculator.PCalcVml(T,P,z)

    'Units conversion
    'Molar volume
    Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
    Set Quantity   = Repository.QuantityByName("Molar volume")
    Vml            = Quantity.Convert(Vml,"cm3/mol","l/mol")

    'Molar mass
    Set MwQty = Repository.QuantityByName("Molar mass")

    'Calculation of the concentrations
    CASN_GelatStarch     = "55100-01-1"
    CASN_ActiveSiteAlpha = "55200-01-6"
    CASN_Malt            = "55521-00-1"
    For i=1 To ThermoCalculator.Compounds.Count
        With ThermoCalculator.Compounds.Items(i-1)
            If (.CasRegistryNumber = CASN_ActiveSiteAlpha) Then
                ipos_ActiveSiteAlpha = i-1
                Mw_ActiveSiteAlpha   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
                C_ActiveSiteAlpha    = z(ipos_ActiveSiteAlpha) * Mw_ActiveSiteAlpha / Vml
                E                    = C_ActiveSiteAlpha  '(g/l)
            ElseIf (.CasRegistryNumber = CASN_GelatStarch) Then
                ipos_GelatStarch     = i-1
                Mw_GelatStarch       = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
                C_GelatStarch        = z(ipos_GelatStarch) * Mw_GelatStarch / Vml
            End If
        End With
    Next
```

Sg = C_GelatStarch \( (g/l) \)

ElseIf (.CasRegistryNumber = CASN_Malt) Then
    ipos_Malt = i-1
    Mw_Malt = MwQty.Convert(.Mw.Value,.Mw.UnitName,"kg/mol")
    C_Malt = z(ipos_Malt) * Mw_Malt / Vml \( (kg/l) \)
End If

'Calculation of the reaction rate
Aalpha = E * As_alpha / C_Malt \ Enzyme activity \( (g/kg\ Malt) \)
CalcR = kg1 * Aalpha * Sg \ Reaction rate for sugar production \( (g\ Starch/l\ s) \)
CalcR = CalcR / Mw_GelatStarch \ Reaction rate for sugar production \( (mol\ Starch/l\ s) \)

'CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/l/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/l/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/l/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/l/s
'Err: Variant - Error code

Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)
    'Reaction rate
    Rate = CalcR(T, P, z)
    'Temperature derivative
    dT = 0.1
    T1 = T + dT
    Rate1 = CalcR(T1, P, z)
    dRatedT = (Rate1 - Rate) / dT
    'Pressure derivative
    dP = 0.1
    P1 = P + dP
    Rate1 = CalcR(T, P1, z)
    dRatedP = (Rate1 - Rate) / dP
End Sub
The VBS code for the (R4) reaction is the following one:

```vbs
Next
    dz = z1(i)*5e-6
    If (dz < 1e-8) Then
        dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j=0 To NC-1
        Tot = Tot + z1(j)
    Next
    For j=0 To NC-1
        z1(j) = z1(j) / Tot
    Next
    Rate1 = CalcR(T, P, z1)
    dRatedN(i) = (Rate1-Rate)/dz
Next
End Sub
```

The VBS code for the (R4) reaction is the following one:

```vbs
'CHECK PROCEDURE
Function CheckRate
    CheckRate = True
End Function

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
    'Model parameters
    kmal_alpha = 0.389 '(kg/U.s)
    kmal_beta  = 0.137 '(kg/U.s)
    R          = 8.31 '(J/mol.K)
    Tlim       = 336 '(K), temperature that separates the two polynomials of the specific activity
    'Calculation of the specific activities
    If (T < Tlim) Then
        As_alpha = -0.00112295*T^3 + 1.091*T^2 - 352.8982*T + 38008.3367
    ElseIf (T >= Tlim) Then
        As_alpha = -0.02729377*T^2 + 17.935*T - 2937.2174
    End If
    If (As_alpha < 0) Then
        As_alpha = 0 'The specific activities cannot be negative
    End If
    'Calculation of the rate
    Rate1 = kmal_alpha*As_alpha
    Rate2 = kmal_beta*As_beta
    Rate = Rate1 + Rate2
End Function
```
If (As_beta < 0) Then As_beta = 0 'The specific activities cannot be negative

'Calculation of the molar volume
Vml = ThermoCalculator.PCalcVml(T,P,z) 'Units conversion

'Molar volume
Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
Set Quantity = Repository.QuantityByName("Molar volume")
Vml = Quantity.Convert(Vml,"cm3/mol","l/mol") 'Molar mass

Set MwQty = Repository.QuantityByName("Molar mass")

'Calculation of the concentrations
CASN_GelatStarch = "55100-01-1"
CASN_ActiveSiteAlpha = "55200-01-6"
CASN_ActiveSiteBeta = "55300-01-1"
CASN_Malt = "55521-00-1"
For i=1 To ThermoCalculator.Compounds.Count
  With ThermoCalculator.Compounds.Items(i-1)
    If (.CasRegistryNumber = CASN_GelatStarch) Then
      ipos_GelatStarch = i-1
      Mw_GelatStarch = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
      C_GelatStarch = z(ipos_GelatStarch) * Mw_GelatStarch / Vml
      Sg = C_GelatStarch ' (g/l)
    ElseIf (.CasRegistryNumber = CASN_ActiveSiteAlpha) Then
      ipos_ActiveSiteAlpha = i-1
      Mw_ActiveSiteAlpha = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
      C_ActiveSiteAlpha = z(ipos_ActiveSiteAlpha) * Mw_ActiveSiteAlpha / Vml
      Ealpha = C_ActiveSiteAlpha ' (g/l)
    ElseIf (.CasRegistryNumber = CASN_ActiveSiteBeta) Then
      ipos_ActiveSiteBeta = i-1
      Mw_ActiveSiteBeta = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
      C_ActiveSiteBeta = z(ipos_ActiveSiteBeta) * Mw_ActiveSiteBeta / Vml
      Ebeta = C_ActiveSiteBeta ' (g/l)
    ElseIf (.CasRegistryNumber = CASN_Malt) Then
      ipos_Malt = i-1
      Mw_Malt = MwQty.Convert(.Mw.Value,.Mw.UnitName,"kg/mol")
      C_Malt = z(ipos_Malt) * Mw_Malt / Vml ' (kg/l)
  End If
  End With
Next

'Calculation of the reaction rate
Aalpha = Ealpha * As_alpha / C_Malt ' Enzyme activity (g/kg Malt)
Abeta = Ebeta * As_beta / C_Malt ' Enzyme activity (g/kg Malt)
CalcR = kmal_alpha * Aalpha * Sg + kmal_beta * Abeta * Sg ' Reaction rate for sugar production (g Starch/l s)
CalcR = CalcR / Mw_GelatStarch ' Reaction rate for sugar production (mol Starch/l s)
End Function

' CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions

--- Results ---
' Rate:  Variant - rate in mol/L/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/L/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/L/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/L/s
'Err: Variant - Error code

Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)

'Reaction rate
Rate = CalcR(T, P, z)

'Temperature derivative
dT = 0.1
T1 = T + dT
Rate1 = CalcR(T1, P, z)
dRatedT = (Rate1-Rate)/dT

'Pressure derivative
dP = 0.1
P1 = P + dP
Rate1 = CalcR(T, P1, z)
dRatedP = (Rate1-Rate)/dP

'Compositions derivatives
NC = ThermoCalculator.Compounds.Count
Dim z1()
ReDim z1(NC-1)
For i=0 To NC-1
    For j=0 To NC-1
        z1(j) = z(j)
        Next
    dz = z1(i)*5e-6
    If (dz < 1e-8) Then
        dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j=0 To NC-1
        Tot = Tot + z1(j)
        Next
    For j=0 To NC-1
        z1(j) = z1(j) / Tot
    Next
End Sub
Next
Rate1 = CalcR(T, P, z1)
dRatedN(i) = (Rate1-Rate)/dz
Next
End Sub

The VBS code for the (R5) reaction is the following one:

'CHECK PROCEDURE
Function CheckRate
    CheckRate = True
End Function

'REACTION RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
    'Model parameters
    kmlt = 0.117 ' (kg/U.s)
    R = 8.31 ' (J/mol.K)
    Tlim = 336 ' (K), temperature that separates the two polynomials of the specific activity
    'Calculation of the specific activity
    If (T < Tlim) Then
        As_alpha = -0.00112295*T^3 + 1.091*T^2 - 352.8982*T + 38008.3367
    ElseIf (T >= Tlim) Then
        As_alpha = -0.02729377*T^2 + 17.935*T - 2937.2174
    End if
    If (As_alpha < 0) Then
        As_alpha = 0 'The specific activities cannot be negative
    'Calculation of the molar volume
    Vml = ThermoCalculator.PCalcVml(T, P, z)
    'Units conversion
    Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
    Set Quantity = Repository.QuantityByName("Molar volume")
    Vml = Quantity.Convert(Vml, "cm3/mol", "l/mol")
    'Molar mass
    Set MwQty = Repository.QuantityByName("Molar mass")
    'Calculation of the concentrations
    CASN_GelatStarch = "55100-01-1"
    CASN_ActiveSiteAlpha = "55200-01-6"
    CASN_Malt = "55521-00-1"
    For i=1 To ThermoCalculator.Compounds.Count
        With ThermoCalculator.Compounds.Items(i-1)
            If (.CasRegistryNumber = CASN_GelatStarch) Then
                ipos_GelatStarch = i-1
                Mw_GelatStarch = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            End If
        End With
    Next

```
C_GelatStarch = z(ipos_GelatStarch) * Mw_GelatStarch / Vml
Sg = C_GelatStarch (g/l)

ElseIf (.CasRegistryNumber = CASN_ActiveSiteAlpha) Then
    ipos_ActiveSiteAlpha = i-1
    Mw_ActiveSiteAlpha = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
    C_ActiveSiteAlpha = z(ipos_ActiveSiteAlpha) * Mw_ActiveSiteAlpha / Vml
    E = C_ActiveSiteAlpha (g/l)
ElseIf (.CasRegistryNumber = CASN_Malt) Then
    ipos_Malt = i-1
    Mw_Malt = MwQty.Convert(.Mw.Value,.Mw.UnitName,"kg/mol")
    C_Malt = z(ipos_Malt) * Mw_Malt / Vml (kg/l)
End If

End With

Next

'Calculation of the reaction rate
Aalpha = E * As_alpha / C_Malt 'Enzyme activity (g/kg Malt)
CalcR = kmlt * Aalpha * Sg 'Reaction rate for sugar production (g Starch/l s)
CalcR = CalcR / Mw_GelatStarch 'Reaction rate for sugar production (mol Starch/l s)
End Function

'CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/l/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/l/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/l/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/l/s
'Err: Variant - Error code

Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)

'Reaction rate
Rate = CalcR(T, P, z)
'Temperature derivative
dT = 0.1
T1 = T + dT
Rate1 = CalcR(T1, P, z)
dRatedT = (Rate1-Rate)/dT

'Pressure derivative
dP = 0.1
P1 = P + dP
Rate1 = CalcR(T, P1, z)
dRatedP = (Rate1-Rate)/dP

Compositions derivatives
```
NC = ThermoCalculator.Compounds.Count
Dim z1()
ReDim z1(NC-1)
For i=0 To NC-1
    For j=0 To NC-1
        z1(j) = z(j)
    Next
    dz = z1(i)*5e-6
    If (dz < 1e-8) Then
        dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j=0 To NC-1
        Tot = Tot + z1(j)
    Next
    For j=0 To NC-1
        z1(j) = z1(j) / Tot
    Next
    Rate1 = CalcR(T, P, z1)
    dRatedN(i) = (Rate1-Rate)/dz
Next
End Sub

The VBS code for the (R6) reaction is the following one:

'CHECK PROCEDURE
Function CheckRate
    CheckRate = True
End Function

'REACTION RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
    'Model parameters
    kdex = 0.317 ' (kg/U.s)
    R = 8.31 ' (J/mol.K)
    Tlim = 336 ' (K), temperature that separates the two polynomials of the specific activity
    'Calculation of the specific activity
    If (T < Tlim) Then
        As_alpha = -0.00112295*T^3 + 1.091*T^2 - 352.8982*T + 38008.3367
    ElseIf (T >= Tlim) Then
        As_alpha = -0.02729377*T^2 + 17.935*T - 2937.2174
    End if
    If (As_alpha < 0) Then As_alpha = 0 'The specific activity cannot be negative
End Function
'Calculation of the molar volume
Vml = ThermoCalculator.PCalcVml(T,P,z)

'Units conversion

'Molar volume
Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
Set Quantity = Repository.QuantityByName("Molar volume")
Vml = Quantity.Convert(Vml,"cm3/mol","l/mol")

'Molar mass
Set MwQty = Repository.QuantityByName("Molar mass")

'Calculation of the concentrations
CASN_GelatStarch = "55100-01-1"
CASN_ActiveSiteAlpha = "55200-01-6"
CASN_Malt = "55521-00-1"
For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
        If (.CasRegistryNumber = CASN_GelatStarch) Then
            ipos_GelatStarch = i-1
            Mw_GelatStarch = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            C_GelatStarch = z(ipos_GelatStarch) * Mw_GelatStarch / Vml
            Sg = C_GelatStarch ' (g/l)
        ElseIf (.CasRegistryNumber = CASN_ActiveSiteAlpha) Then
            ipos_ActiveSiteAlpha = i-1
            Mw_ActiveSiteAlpha = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            C_ActiveSiteAlpha = z(ipos_ActiveSiteAlpha) * Mw_ActiveSiteAlpha / Vml
            E = C_ActiveSiteAlpha ' (g/l)
        ElseIf (.CasRegistryNumber = CASN_Malt) Then
            ipos_Malt = i-1
            Mw_Malt = MwQty.Convert(.Mw.Value,.Mw.UnitName,"kg/mol")
            C_Malt = z(ipos_Malt) * Mw_Malt / Vml ' (kg/l)
    End If
    End With
Next

'Calculation of the reaction rate
Aalpha = E * As_alpha / C_Malt ' Enzyme activity (g/kg Malt)
CalcR = kdex * Aalpha * Sg ' Reaction rate for sugar production (g Starch/l s)
CalcR = CalcR / Mw_GelatStarch ' Reaction rate for sugar production (mol Starch/l s)

End Function

'CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/l/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/L/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/L/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/L/s
'Err: Variant - Error code

Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)
  'Reaction rate
  Rate = CalcR(T, P, z)
  'Temperature derivative
  dT = 0.1
  T1 = T + dT
  Rate1 = CalcR(T1, P, z)
  dRatedT = (Rate1 - Rate) / dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z)
  dRatedP = (Rate1 - Rate) / dP
  'Compositions derivatives
  NC = ThermoCalculator.Compounds.Count
  Dim z1()
  ReDim z1(NC - 1)
  For i = 0 To NC - 1
    For j = 0 To NC - 1
      z1(j) = z(j)
    Next
    dz = z1(i) * 5e-6
    If (dz < 1e-8) Then
      dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j = 0 To NC - 1
      Tot = Tot + z1(j)
    Next
    z1(j) = z1(j) / Tot
  Next
  Rate1 = CalcR(T, P, z1)
  dRatedN(i) = (Rate1 - Rate) / dz
  Next
End Sub
The VBS code for the (R7) reaction is the following one:

```
'CHECK PROCEDURE
Function CheckRate
  CheckRate = True
End Function

'REACTION RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
  'Model parameters
  k_g1 = 2.9E-8 ' (kg/U.s)
  R    = 8.31 ' (J/mol.K)
  Tlim = 336 ' (K), temperature that separates the two polynomials of the specific activity

  'Calculation of the specific activity
  If (T < Tlim) Then
    As_alpha = -0.00112295*T^3 + 1.091*T^2 - 352.8982*T + 38008.3367
  ElseIf (T >= Tlim) Then
    As_alpha = -0.02729377*T^2 + 17.935*T - 2937.2174
  End If

  If (As_alpha < 0) Then As_alpha = 0 ' The specific activity cannot be negative

  'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)

  'Units conversion
  'Molar volume
  Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
  Set Quantity = Repository.QuantityByName("Molar volume")
  Vml = Quantity.Convert(Vml,"cm3/mol","l/mol")

  'Molar mass
  Set MwQty = Repository.QuantityByName("Molar mass")

  'Calculation of the concentrations
  CASN_Dextrin = "55100-02-2"
  CASN_ActiveSiteAlpha = "55200-01-6"
  CASN_Malt = "55521-00-1"
  For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
      If (.CasRegistryNumber = CASN_Dextrin) Then
        ipos_Dextrin = i-1
        Mw_Dextrin = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
        C_Dextrin = z(ipos_Dextrin) * Mw_Dextrin / Vml
        D = C_Dextrin '(g/l)
      ElseIf (.CasRegistryNumber = CASN_ActiveSiteAlpha) Then
        ipos_ActiveSiteAlpha = i-1
        Mw_ActiveSiteAlpha = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
        C_ActiveSiteAlpha = z(ipos_ActiveSiteAlpha) * Mw_ActiveSiteAlpha / Vml
    End If
  Next

```

E  = C_ActiveSiteAlpha \( \text{g/l} \)

ElseIf (.CasRegistryNumber = CASN_Malt) Then
  ipos_Malt = i-1
  Mw_Malt   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"kg/mol")
  C_Malt    = z(ipos_Malt) * Mw_Malt / Vml \( \text{kg/l} \)
End If

End With

'Calculation of the reaction rate
Aalpha = E * As_alpha / C_Malt 'Enzyme activity (g/kg Malt)
CalcR  = k_gl * Aalpha * D 'Reaction rate for sugar production (g Dextrin/l s)
CalcR  = CalcR / Mw_Dextrin 'Reaction rate for sugar production (mol Dextrin/l s)

End Function

'CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/l/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/l/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/l/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/l/s
'Err: Variant - Error code

Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)

  'Reaction rate
  Rate = CalcR(T, P, z)

  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z)
  dRatedT = (Rate1-Rate)/dT

  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z)
  dRatedP = (Rate1-Rate)/dP

  'Compositions derivatives
  NC = ThermoCalculator.Compounds.Count
  Dim z1()
  ReDim z1(NC-1)
  For i=0 To NC-1
    For j=0 to NC-1
      z1(j) = z(j)
    Next j
  Next i

End Sub
Next

dz = z1(i)*5e-6

If (dz < 1e-8) Then
   dz = 1e-8
End If

z1(i) = z1(i) + dz

Tot = 0

For j=0 to NC-1
   Tot = Tot + z1(j)
Next

For j=0 to NC-1
   z1(j) = z1(j) / Tot
Next

Rate1 = CalcR(T, P, z1)

dRatedN(i) = (Rate1-Rate)/dz

End Sub

The VBS code for the (R8) reaction is the following one:

'CHECK PROCEDURE

Function CheckRate
   CheckRate = True
End Function

'REACTON RATE CALCULATION FUNCTION

Function CalcR(T, P, z)
   'Model parameters
   kmal_alpha = 1.2E-7 ' (kg/U.s)
   kmal_beta  = 8.4E-8 ' (kg/U.s)
   R          = 8.31 ' (J/mol.K)
   Tlim       = 336 ' (K), temperature that separates the two polynomials of the specific activity

   'Calculation of the specific activities
   If (T < Tlim) Then
      As_alpha = -0.00112295*T^3 + 1.091*T^2 - 352.8982*T + 38008.3367
   ElseIf (T >= Tlim) Then
      As_alpha = -0.02729377*T^2 + 17.935*T - 2937.2174
   End if

   If (As_alpha < 0) Then As_alpha = 0 ' The specific activities cannot be negative

   'Calculation of the specific activities
If (As_beta < 0) Then As_beta = 0

'Calculation of the molar volume
Vml = ThermoCalculator.PCalcVml(T,P,z)

'Units conversion

'Molar volume
Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
Set Quantity = Repository.QuantityByName("Molar volume")
Vml = Quantity.Convert(Vml,"cm3/mol","l/mol")

'Molar mass
Set MwQty = Repository.QuantityByName("Molar mass")

'Calculation of the concentrations
CASN_Dextrin = "55100-02-2"
CASN_ActiveSiteAlpha = "55200-01-6"
CASN_ActiveSiteBeta = "55300-01-1"
CASN_Malt = "55521-00-1"

For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
        If (.CasRegistryNumber = CASN_Dextrin) Then
            ipos_Dextrin = i-1
            Mw_Dextrin = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            C_Dextrin = z(ipos_Dextrin) * Mw_Dextrin / Vml
            D = C_Dextrin ' (g/l)
        ElseIf (.CasRegistryNumber = CASN_ActiveSiteAlpha) Then
            ipos_ActiveSiteAlpha = i-1
            Mw_ActiveSiteAlpha = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            C_ActiveSiteAlpha = z(ipos_ActiveSiteAlpha) * Mw_ActiveSiteAlpha / Vml
            Ealpha = C_ActiveSiteAlpha ' (g/l)
        ElseIf (.CasRegistryNumber = CASN_ActiveSiteBeta) Then
            ipos_ActiveSiteBeta = i-1
            Mw_ActiveSiteBeta = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            C_ActiveSiteBeta = z(ipos_ActiveSiteBeta) * Mw_ActiveSiteBeta / Vml
            Ebeta = C_ActiveSiteBeta ' (g/l)
        ElseIf (.CasRegistryNumber = CASN_Malt) Then
            ipos_Malt = i-1
            Mw_Malt = MwQty.Convert(.Mw.Value,.Mw.UnitName,"kg/mol")
            C_Malt = z(ipos_Malt) * Mw_Malt / Vml ' (kg/l)
        End If
    End With
Next

'Calculation of the reaction rate
Aalpha = Ealpha * As_alpha / C_Malt ' Enzyme activity (g/kg Malt)
Abeta  = Ebeta * As_beta / C_Malt ' Enzyme activity (g/kg Malt)
CalcR  = kmal_alpha * Aalpha * D + kmal_beta * Abeta * D ' Reaction rate for sugar production (g Dextrin/l s)
CalcR  = CalcR / Mw_Dextrin ' Reaction rate for sugar production (mol Dextrin/l s)
End Function

' CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/l/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/l/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/l/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/l/s
'Err: Variant - Error code

Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)

' Reaction rate
Rate = CalcR(T, P, z)

'Temperature derivative
dT = 0.1
T1 = T + dT
Rate1 = CalcR(T1, P, z)
dRatedT = (Rate1 - Rate) / dT

' Pressure derivative
dP = 0.1
P1 = P + dP
Rate1 = CalcR(T, P1, z)
dRatedP = (Rate1 - Rate) / dP

' Compositions derivatives
NC = ThermoCalculator.Compounds.Count
Dim z1()
ReDim z1(NC - 1)
For i = 0 To NC - 1
    For j = 0 To NC - 1
        z1(j) = z(j)
    Next
    dz = z1(i) * 5e-6
    If (dz < 1e-8) Then
        dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j = 0 To NC - 1
        Tot = Tot + z1(j)
    Next
    For j = 0 To NC - 1
        z1(j) = z1(j) / Tot
Next
The VBS code for the (R9) reaction is the following one:

```vbs
' CHECK PROCEDURE
Function CheckRate
    CheckRate = True
End Function

' REACTION RATE CALCULATION FUNCTION
Function CalcR(T, P, z)
    ' Model parameters
    k_mlt = 1.5E-8 ' (kg/U.s)
    R     = 8.31  ' (J/mol.K)
    Tlim  = 336   ' (K), temperature that separates the two polynomials of the specific activity
    ' Calculation of the specific activity
    If (T < Tlim) Then
        As_alpha = -0.00112295*T^3 + 1.091*T^2 - 352.8982*T + 38008.3367
    ElseIf (T >= Tlim) Then
        As_alpha = -0.02729377*T^2 + 17.935*T - 2937.2174
    End If
    If (As_alpha < 0) Then
        As_alpha = 0 ' The specific activity cannot be negative
    End If
    ' Calculation of the molar volume
    Vml = ThermoCalculator.PCalcVml(T,P,z)
    ' Units conversion
    Set Repository = CreateObject("CverStarDustRepository.StarDust_CVER_Repository")
    Set Quantity   = Repository.QuantityByName("Molar volume")
    Vml            = Quantity.Convert(Vml,"cm3/mol","l/mol")
    ' Molar mass
    Set MwQty = Repository.QuantityByName("Molar mass")
    ' Calculation of the concentrations
    CASN_Dextrin   = "55100-02-2"
    CASN_ActiveSiteAlpha = "55200-01-6"
    CASN_Malt     = "55521-00-1"
    For i=1 To ThermoCalculator.Compounds.Count
        With ThermoCalculator.Compounds.Items(i-1)
            If (.CasRegistryNumber = CASN_Dextrin) Then
                ipos_Dextrin = i-1
                Mw_Dextrin   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
            ' Other cases (CASN_ActiveSiteAlpha, CASN_Malt)
        End With
    Next
```

Next
Rate1 = CalcR(T, P, z1)
dRatedN(i) = (Rate1-Rate)/dz
Next
End Sub
C_Dextrin = z(ipos_Dextrin) * Mw_Dextrin / Vml
D = C_Dextrin

ElseIf (.CasRegistryNumber = CASN_ActiveSiteAlpha) Then
    ipos_ActiveSiteAlpha = i-1
    Mw_ActiveSiteAlpha = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
    C_ActiveSiteAlpha = z(ipos_ActiveSiteAlpha) * Mw_ActiveSiteAlpha / Vml
    E = C_ActiveSiteAlpha

ElseIf (.CasRegistryNumber = CASN_Malt) Then
    ipos_Malt = i-1
    Mw_Malt = MwQty.Convert(.Mw.Value,.Mw.UnitName,"kg/mol")
    C_Malt = z(ipos_Malt) * Mw_Malt / Vml 'kg/l)
End If

End With

Next

'Calculation of the reaction rate
Aalpha = E * As_alpha / C_Malt  'Enzyme activity (g/kg Malt)
CalcR = k_mlt * Aalpha * D   'Reaction rate for sugar production (g Dextrin/l s)
CalcR = CalcR / Mw_Dextrin 'Reaction rate for sugar production (mol Dextrin/l s)
End Function

'CALCULATION PROCEDURE
'T: Variant - Temperature (K)
'P: Variant - Pressure (atm)
'z: Variant - Molar fractions
'--- Results ---
'Rate: Variant - rate in mol/l/s
'dRatedT: Variant - rate derivative with the respect to temperature in mol/l/s/K
'dRatedP: Variant - rate derivative with the respect to pressure in mol/l/s/atm
'dRatedN: Variant - rate derivative with the respect to number of moles in mol/l/s
'Err: Variant - Error code
Sub CalcRate(T, P, z, Rate, dRatedT, dRatedP, dRatedN, Err)
    'Reaction rate
    Rate = CalcR(T, P, z)

    'Temperature derivative
    dT = 0.1
    T1 = T + dT
    Rate1 = CalcR(T1, P, z)
    dRatedT = (Rate1-Rate)/dT

    'Pressure derivative
    dP = 0.1
    P1 = P + dP
    Rate1 = CalcR(T, P1, z)
    dRatedP = (Rate1-Rate)/dP

    'Compositions derivatives
End Sub
NC = ThermoCalculator.Compounds.Count
Dim z1()
ReDim z1(NC-1)
For i=0 To NC-1
    For j=0 To NC-1
        z1(j) = z(j)
    Next
    dz = z1(i)*5e-6
    If (dz < 1e-8) Then
        dz = 1e-8
    End If
    z1(i) = z1(i) + dz
    Tot = 0
    For j=0 To NC-1
        Tot = Tot + z1(j)
    Next
    For j=0 To NC-1
        z1(j) = z1(j) / Tot
    Next
    Rate1 = CalcR(T, P, z1)
    dRatedN(i) = (Rate1-Rate)/dz
Next
End Sub
7. Simulation

7.1. Process description

The reactor used for the hydrolysis of starch is a single-phase liquid reactor.

The initial mass in the reactor is obtained from the experimental data. The initial load is the same for the three cases studied. In [BRA03], the concentrations are given in g/kg\textsubscript{malt} or in U/kg\textsubscript{malt}, which means a quantity of malt. Thus, a usual quantity of 20 kg of malt is chosen in the simulation to determine the initial loads of each component. This quantity of malt corresponds to a usual load of liquid of 70 kg. Regarding the grain-size distribution of the starch, it is considered that the starch is composed of 95 wt. % of big grains and 5 wt. % of small grains. Furthermore, according to experimental data, the usual quantity of water and malt used are 70 kg and 20 kg, respectively.

The following table presents the experiments concentration from [BRA03] and the corresponding initial loads used in the simulations.

<table>
<thead>
<tr>
<th>Initial conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial compositions</th>
<th>Concentration [BRA03]</th>
<th>Load (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Maltose</td>
<td>5 g/kg\textsubscript{malt}</td>
<td>0.100</td>
</tr>
<tr>
<td>Glucose</td>
<td>4 g/kg\textsubscript{malt}</td>
<td>0.080</td>
</tr>
<tr>
<td>Small grains of non gelatinized starch</td>
<td>113.5 g/kg\textsubscript{malt}</td>
<td>0.1135</td>
</tr>
<tr>
<td>Big grains of non gelatinized starch</td>
<td></td>
<td>2.1565</td>
</tr>
<tr>
<td>(\alpha) sites</td>
<td>210 U/kg\textsubscript{malt}</td>
<td>4.200</td>
</tr>
<tr>
<td>(\beta) sites</td>
<td>380 U/kg\textsubscript{malt}</td>
<td>7.600</td>
</tr>
<tr>
<td>Malt</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Other component</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The experimental runs studied in this example (runs E1, E7 and E10) follow different temperature profiles (see the following figure). To describe this in BatchReactor it has been chosen to use several “Specified TR without thermal device” steps. Depending on the temperature profiles of the experiments these steps are at constant temperature or at given temperature profile. The event “Time spent since the beginning of the step” is used to stop each step. The corresponding times are also extracted from the experiments temperature profiles.

![Temperature profile of runs E1, E7 and E10 (BRA03)](image)

The following screen shot presents the simulation of the Run E1 experiment. The scenario is presented on the left part of this screen shot and the flowsheet on the right part.
7.2. Results

Comparisons between concentration profiles obtained with BatchReactor software and information given by [BRA03] are provided in the next paragraphs.

7.2.1. Run E1

Time evolution of active sites concentration (run E1)

Time evolution of enzymes activities concentration (run E1)
Time evolution of products concentrations (run E1)

- Glucose - Simulation
- Glucose [BRA03]
- Maltose - Simulation
- Maltose [BRA03]
- Maltotriose - Simulation
- Maltotriose [BRA03]
- Dextrin - Simulation
- Dextrin [BRA03]
- Temperature

Concentration (g/kg mann) vs. Time (min)
7.2.2. Run E7

Time evolution of active sites concentration (run E7)

Time evolution of enzymes activities concentration (run E7)
Time evolution of products concentration (run E7)

- Glucose - Simulation
- Glucose [BRA03]
- Maltose - Simulation
- Maltose [BRA03]
- Maltotriose - Simulation
- Maltotriose [BRA03]
- Dextrin - Simulation
- Série8
- Temperature

Concentration (g/kg mixture) vs. Time (min)

Temperature (°C)
7.2.3. Run E10

**Time evolution of active sites concentration (run E10)**

- **Alpha active sites - Simulation**
- **Alpha active sites [BRA03]**
- **Beta active sites - Simulation**
- **Beta active sites [BRA03]**
- **Temperature**

**Time evolution of enzymes activities concentration (run E10)**

- **Alpha-amylase - Simulation**
- **Alpha-amylase [BRA03]**
- **Beta-amylase - Simulation**
- **Beta-amylase [BRA03]**
- **Temperature**
Time evolution of products concentration (run E10)

- Glucose - Simulation
- Glucose [BRA03]
- Maltose - Simulation
- Maltose [BRA03]
- Maltotriose - Simulation
- Maltotriose [BRA03]
- Dextrin - Simulation
- Dextrin [BRA03]

Concentration (g/kg) vs. Temperature (°C)

Concentration (g/kg) vs. Time (min)
8. REFERENCES


9. NOMENCLATURE

\( a_a \)  Global activity of \( \alpha \)-amylase enzyme \( \text{U/kg}_{\text{malt}} \)

\( a_\beta \)  Global activity of \( \beta \)-amylase enzyme \( \text{U/kg}_{\text{malt}} \)

\( a_s \)  Relative specific enzyme activity (-)

\([D]\)  Dextrin concentration \( \text{g/kg}_{\text{malt}} \)

\([E_a]\)  Active \( \alpha \)-amylase enzyme site concentration \( \text{g/kg}_{\text{malt}} \)

\([E_\beta]\)  Active \( \beta \)-amylase enzyme site concentration \( \text{g/kg}_{\text{malt}} \)

\( E_t \)  Activation energy \( \text{J/mol} \)

\( k_{\alpha,\text{mat}} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k'_{\alpha,\text{mat}} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k_{\beta,\text{mat}} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k'_{\beta,\text{mat}} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k_{da} \)  Pre-exponential factor \( s^{-1} \)

\( k_{db} \)  Pre-exponential factor \( s^{-1} \)

\( k_{\text{dex}} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k_{g1} \)  Pre-exponential factor \( s^{-1} \)

\( k_{g2} \)  Pre-exponential factor \( s^{-1} \)

\( k_{gt} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k'_{gt} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k_{\text{mit}} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k'_{\text{mit}} \)  Kinetic factor \( \text{kg/(U.s)} \)

\( k_{sg} \)  Pre-exponential factor \( s^{-1} \)

\( R \)  Perfect gas constant \( \text{J/(mol/K)} \)

\( r_{da} \)  Rate of reaction \( \text{U/(kg.s)} \)

\( r_{d\beta} \)  Rate of reaction \( \text{U/(kg.s)} \)

\( r_{\text{dex}} \)  Rate of reaction \( \text{g/(kg}_{\text{malt}}\text{s)} \)

\( r_{g} \)  Rate of reaction \( \text{g/(kg}_{\text{malt}}\text{s)} \)

\( r_{gt} \)  Rate of reaction \( \text{g/(kg}_{\text{malt}}\text{s)} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r'_{gl}$</td>
<td>Rate of reaction</td>
<td>g/(kg_malt s)</td>
</tr>
<tr>
<td>$r_{mal}$</td>
<td>Rate of reaction</td>
<td>g/(kg_malt s)</td>
</tr>
<tr>
<td>$r'_{mal}$</td>
<td>Rate of reaction</td>
<td>g/(kg_malt s)</td>
</tr>
<tr>
<td>$r_{mittel}$</td>
<td>Rate of reaction</td>
<td>g/(kg_malt s)</td>
</tr>
<tr>
<td>$r'_{mittel}$</td>
<td>Rate of reaction</td>
<td>g/(kg_malt s)</td>
</tr>
<tr>
<td>$r_{sg}$</td>
<td>Rate of reaction</td>
<td>g/(kg_malt s)</td>
</tr>
<tr>
<td>$[S_g]$</td>
<td>Gelatinized starch concentration</td>
<td>g/kg_malt</td>
</tr>
<tr>
<td>$[S_S]$</td>
<td>Big non gelatinized starch grains concentration</td>
<td>g/kg_malt</td>
</tr>
<tr>
<td>$[S_{SS}]$</td>
<td>Small non gelatinized starch grains concentration</td>
<td>g/kg_malt</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Threshold temperature</td>
<td>°C</td>
</tr>
</tbody>
</table>