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*

Energy

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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 ot 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.

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2. Reaction mechanism

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

- ✓ Big grains of non gelatinized starch forming gelatinized starch:

$$Big\ grains\ of\ non\ gelatinized\ starch \xrightarrow{Temperature} Gelatinized\ starch \tag{R1}$$

- ✓ Small grains of non gelatinized starch forming gelatinized starch:

$$Small\ grains\ of\ non\ gelatinized\ starch \xrightarrow{Temperature} Gelatinized\ starch \tag{R2}$$

- ✓ Gelatinized starch forming glucose:

$$Gelatinized\ starch + n\ water \xrightarrow{\alpha-amylase} n\ Glucose$$

For example,

$$(C_6H_{10}O_5)_n + n\ H_2O \xrightarrow{\alpha-amylase} n\ C_6H_{12}O_6 \tag{R3}$$

- ✓ Gelatinized starch forming maltose:

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

For example,

$$(C_6H_{10}O_5)_n + \frac{n}{2}\ H_2O \xrightarrow{\alpha/\beta-amylase} \frac{n}{2}\ C_{12}H_{22}O_{11} \tag{R4}$$

- ✓ Gelatinized starch forming maltotriose:

$$Gelatinized\ starch + \frac{n}{3}\ Water \xrightarrow{\alpha-amylase} \frac{n}{3}\ Maltotriose$$

For example,

$$(C_6H_{10}O_5)_n + \frac{n}{3}\ H_2O \xrightarrow{\alpha-amylase} \frac{n}{3}\ C_{18}H_{32}O_{16} \tag{R5}$$

- ✓ Gelatinized starch forming dextrin:

$$Gelatinized\ starch \xrightarrow{\alpha-amylase} x\ Dextrin$$

For example,

$$(C_6H_{10}O_5)_n \xrightarrow{\alpha-amylase} x\,(C_6H_{10}O_5)_{n/x} \quad \text{(R6)}$$

- ✓ Dextrin forming glucose:

$$Dextrin + \frac{n}{x}\,Water \xrightarrow{\alpha-amylase} \frac{n}{x}\,Glucose$$

For example,

$$(C_6H_{10}O_5)_{n/x} + \frac{n}{x}\,H_2O \xrightarrow{\alpha-amylase} \frac{n}{x}\,C_6H_{12}O_6 \quad \text{(R7)}$$

- ✓ Dextrin forming maltose:

$$Dextrin + \frac{n}{2x}\,Water \xrightarrow{\alpha/\beta-amylase} \frac{n}{2x}\,Maltose$$

For example,

$$(C_6H_{10}O_5)_{n/x} + \frac{n}{2x}\,H_2O \xrightarrow{\alpha/\beta-amylase} \frac{n}{2x}\,C_{12}H_{22}O_{11} \quad \text{(R8)}$$

- ✓ Dextrin forming maltotriose:

$$Dextrin + \frac{n}{3x}\,Water \xrightarrow{\alpha-amylase} \frac{n}{3x}\,Maltotriose$$

For example,

$$(C_6H_{10}O_5)_{n/x} + \frac{n}{3x}\,H_2O \xrightarrow{\alpha-amylase} \frac{n}{3x}\,C_{18}H_{32}O_{16} \quad \text{(R9)}$$

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.

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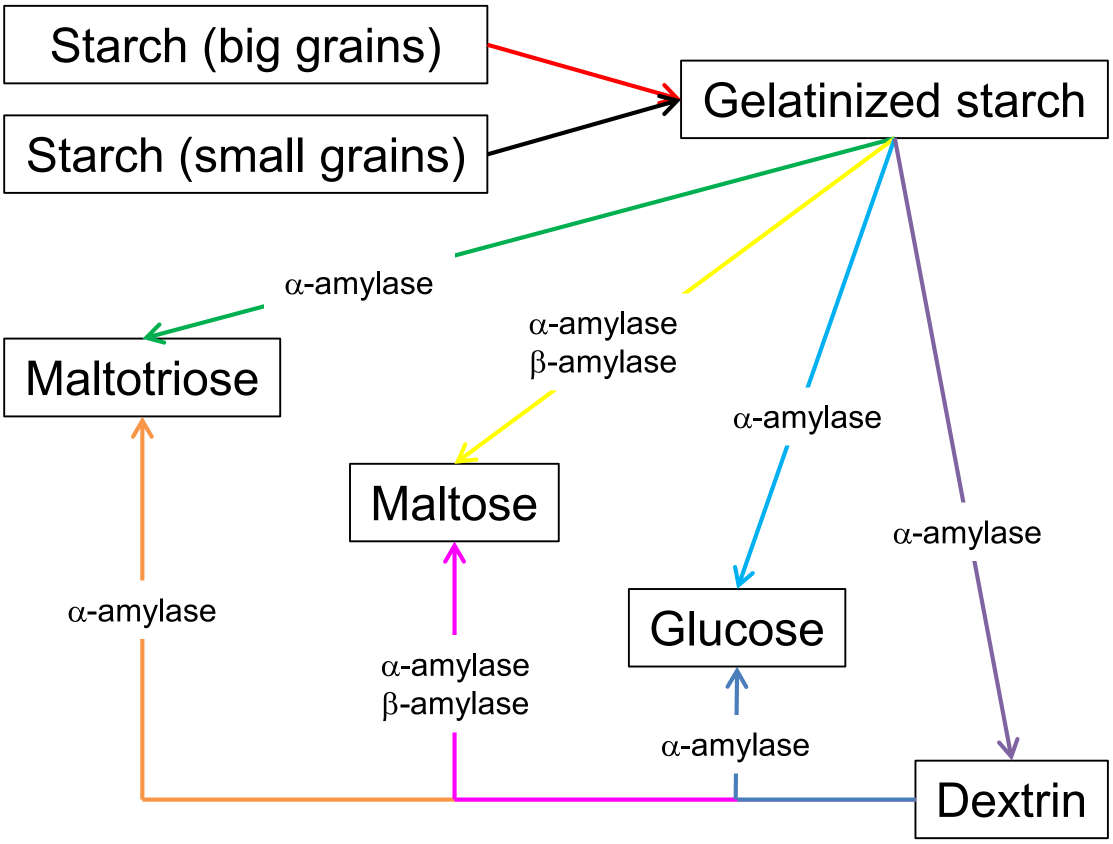
All of these reactions can be represented by the following diagram.



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

- ✓ Active α sites forming inactive α sites:

$$One\ active\ \alpha\ site\ \longrightarrow One\ inactive\ \alpha\ site \qquad \text{(R10)}$$

- ✓ Active β sites forming inactive β sites

$$One\ active\ \beta\ site\ \longrightarrow One\ inactive\ \beta\ site \qquad \text{(R11)}$$

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3. Components

Components which are taken into account in the simulation are:

Name	CAS[(1)] number
Water[(*)]	7732-18-5
Glucose[(*)]	50-99-7
Maltose[(*)]	57-50-1
Maltotriose	
Dextrin	
Small grains of non gelatinized starch	
Big grains of non gelatinized starch	
Gelatinized starch	
Active α site	
Inactive α site	
Active β site	
Inactive β site	
Malt	

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[(1)] number (arbitrary numbers)
- ✓ Molecular weight
- ✓ Liquid density (same value as water)

The other compounds (active and inactive α site, active and inactive β 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[(1)] 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

$$Ln(P^0) = -30 \quad \text{(Equation 101)}$$

- ✓ 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.

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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:

$$r_g = k_{g1} \times \exp\left(\frac{-E_{g1}}{RT}\right)[S_S] \quad for\ T < 60°C$$
$$r_g = k_{g2} \times \exp\left(\frac{-E_{g2}}{RT}\right)[S_S] \quad for\ T > 60°C \quad \text{(R1)}$$

- ✓ Rate of small grains of starch gelatinization:

$$r_{sg} = 0 \quad for\ T < 60°C$$
$$r_{sg} = k_{sg} \times \exp\left(\frac{-E_{sg}}{RT}\right)[S_{SS}] \quad for\ T > 60°C \quad \text{(R2)}$$

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:

$$r_{gl} = k_{gl} \times a_\alpha \times [S_g] \quad \text{(R3)}$$

- ✓ Rate of gelatinized starch forming maltose:

$$r_{mal} = k_{\alpha,mal} \times a_\alpha \times [S_g] + k_{\beta,mal} \times a_\beta \times [S_g] \quad \text{(R4)}$$

- ✓ Rate of gelatinized starch forming maltotriose:

$$r_{mlt} = k_{mlt} \times a_\alpha \times [S_g] \quad \text{(R5)}$$

- ✓ Rate of gelatinized starch forming dextrin:

$$r_{dex} = k_{dex} \times a_{\alpha} \times [S_g] \quad \text{(R6)}$$

- ✓ Rate of dextrin forming glucose:

$$r'_{gl} = k'_{gl} \times a_{\alpha} \times [D] \quad \text{(R7)}$$

- ✓ Rate of dextrin forming maltose:

$$r'_{mal} = k'_{\alpha,mal} \times a_{\alpha} \times [D] + k'_{\beta,mal} \times a_{\beta} \times [D] \quad \text{(R8)}$$

- ✓ Rate of dextrin forming maltotriose:

$$r'_{mlt} = k'_{mlt} \times a_{\alpha} \times [D] \quad \text{(R9)}$$

- ✓ Rate of denaturation of active sites:

$$r_{d\alpha} = k_{d\alpha} \times \exp\left(\frac{-E_{d\alpha}}{RT}\right)[E_{\alpha}] \quad \text{(R10)}$$

$$r_{d\beta} = k_{d\beta} \times \exp\left(\frac{-E_{d\beta}}{RT}\right)[E_{\beta}] \quad \text{(R11)}$$

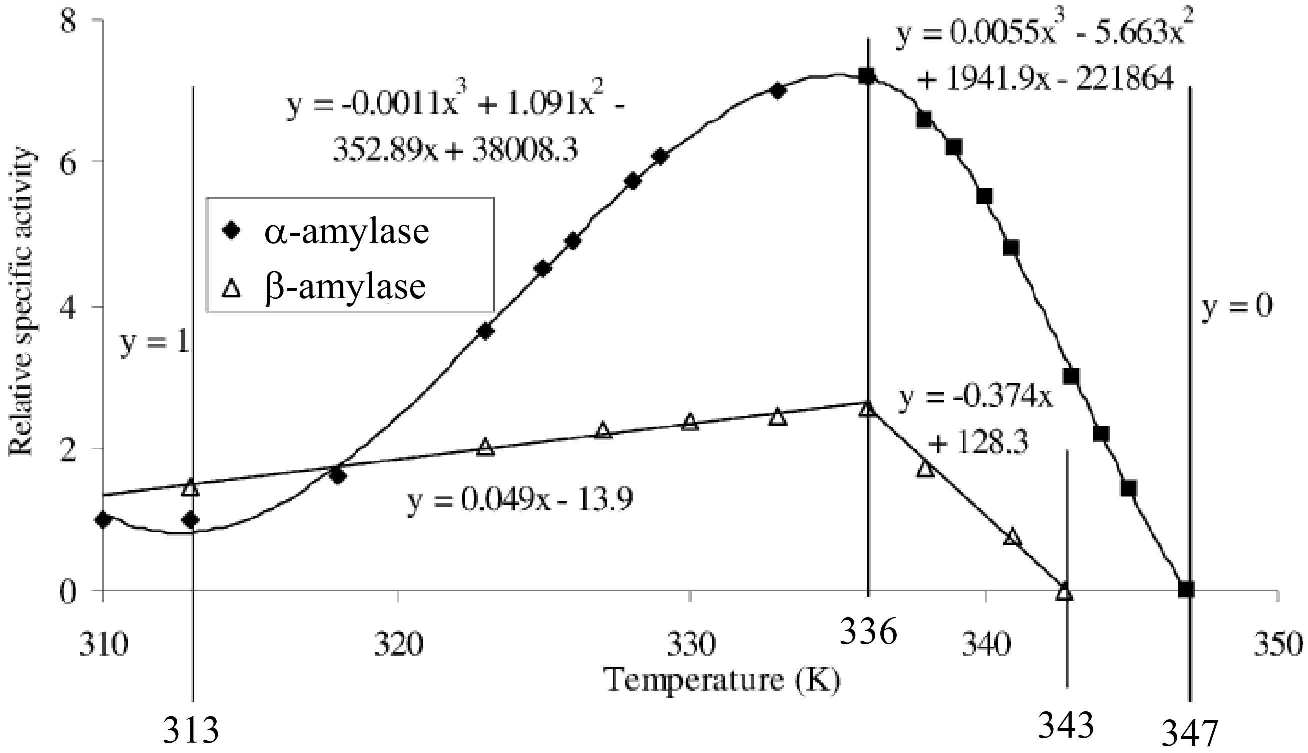
- ✓ Enzyme activities a_{α} and a_{β}:

$$a_{\alpha} = [E_{\alpha}] \times a_S(T)$$

$$a_{\beta} = [E_{\beta}] \times a_S(T)$$

The relative specific enzyme activity $a_S(T)$ 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 α- and β-amylases



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

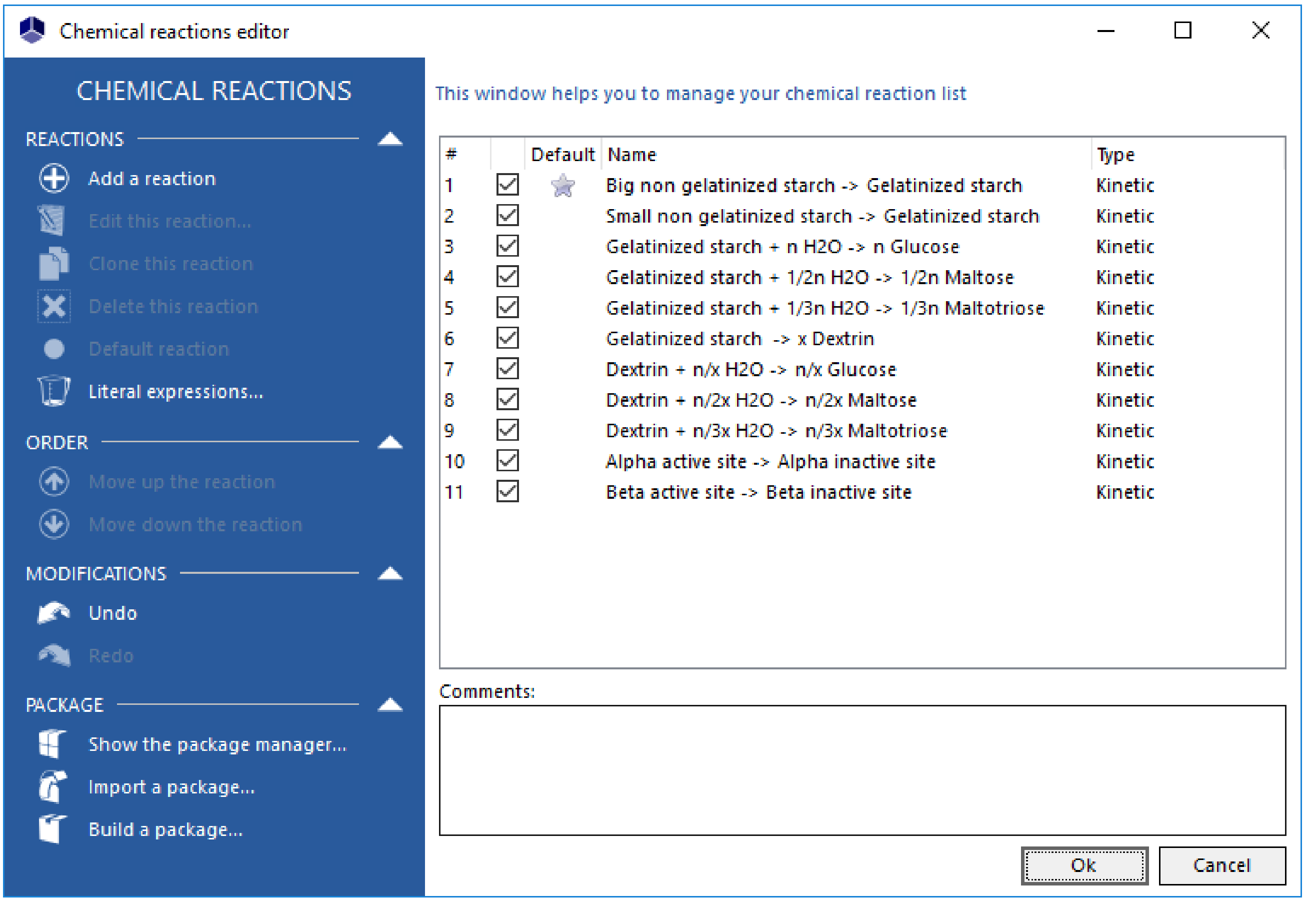
k_{gl}	$k_{\alpha,mal}$	$k_{\beta,mal}$	k_{mlt}	k_{dex}	k'_{gl}	$k'_{\alpha,mal}$	$k'_{\beta,mal}$	k'_{mlt}
(kg/(U.s))								
0.023	0.389	0.137	0.117	0.317	$2.9e^{-8}$	$1.2e^{-7}$	$8.4e^{-8}$	$1.5e^{-8}$

k_{g1}	k_{g2}	k_{sg}	$k_{d\alpha}$	$k_{d\beta}$
(s^{-1})				
$5.7e^{31}$	$3.1e^{14}$	$4.18e^{35}$	$6.9e^{30}$	$7.6e^{60}$

E_{g1}	E_{g2}	E_{sg}	$E_{d\alpha}$	$E_{d\beta}$
(J/mol)				
220 600	108 300	253 600	224 200	410 700

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 screen shot.



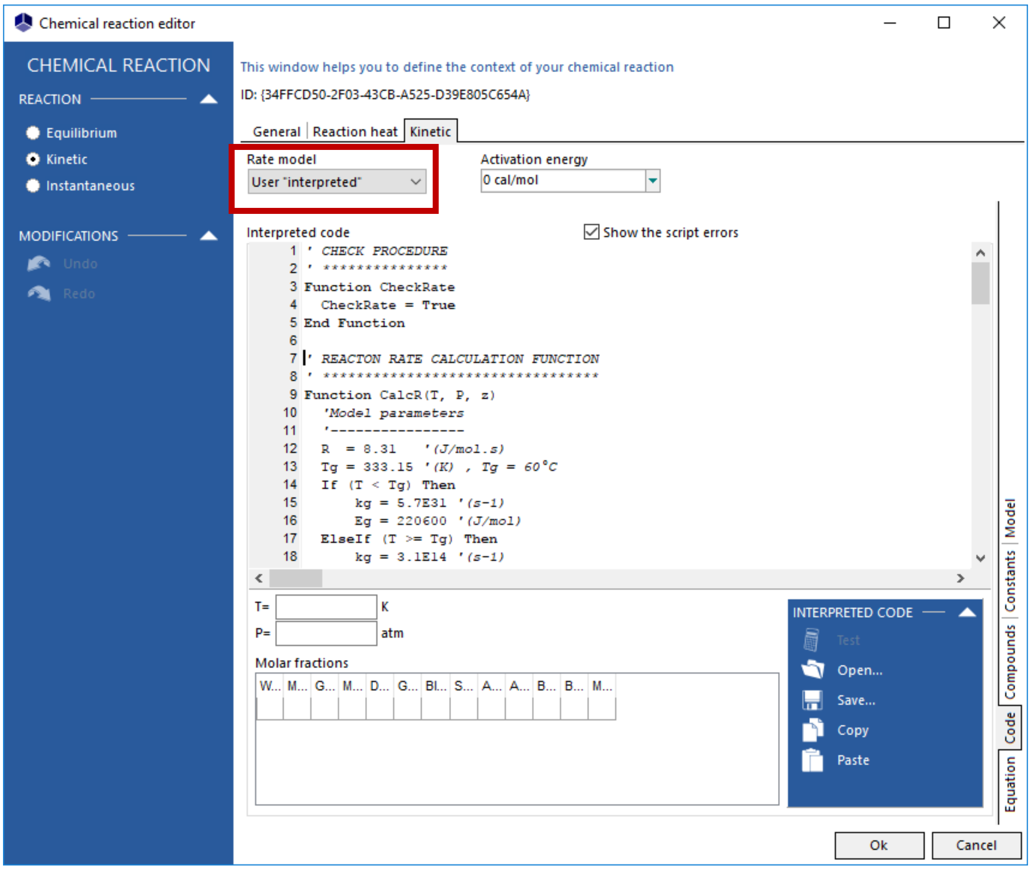
The two reactions of denaturation of active sites follow “classic” Arrhenius laws. Thus, they are described with the standard Simulis Reactions interface. Regarding the other reactions, user “interpreted” kinetic rate model was used to implement mathematical models presented by [BRA03] as shown on the 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/t0aew7h6(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


'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
  'Model parameters
  R  = 8.31   '(J/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)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
```

```
  '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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
  'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    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

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
  'Model parameters
  ksg = 4.18E35 '(s-1)
  Esg = 253600  '(J/mol)
  R   = 8.31    '(J/mol.s)
  'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
  '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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
  'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
```



```
  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, VmQty, MwQty)
    dRatedN(i) = (Rate1-Rate)/dz
  Next
End Sub
```

The VBS code for the (R3) reaction is the following one:

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

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
  '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
  'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
  '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
           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
```

```
    End With
  Next
  'Calculation of the reaction rate
  Aalpha = E * As_alpha / C_Malt     'Enzyme activity (g/kg Malt)
  CalcR  = kgl * 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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
  'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    dRatedN(i) = (Rate1-Rate)/dz
  Next
End Sub
```

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

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

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
  '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 (T < Tlim) Then
      As_beta = 0.0495*T - 13.993
  ElseIf (T >= Tlim) then
      As_beta = -0.37416*T + 128.274
  End If
  If (As_alpha < 0) Then As_alpha = 0 'The specific activities cannot be negative
  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)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")

 '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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
 'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    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

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
 '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)
  'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
  '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  = 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, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    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

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
 '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
  'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
  '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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
  'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
```

```
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    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

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
 'Model parameters
  k_gl = 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)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
  '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
           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  = 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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
  'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    dRatedN(i) = (Rate1-Rate)/dz
```

```
  Next
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, VmQty, MwQty)
 '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 (T < Tlim) Then
      As_beta = 0.0495*T - 13.993
  ElseIf (T >= Tlim) Then
      As_beta = -0.37416*T + 128.274
  End if
  If (As_alpha < 0) Then As_alpha = 0 'The specific activities cannot be negative
  If (As_beta < 0) Then As_beta  = 0
 'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
 '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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
  'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
```

```
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    dRatedN(i) = (Rate1-Rate)/dz
  Next
End Sub
```

The VBS code for the (R9) reaction is the following one:

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

'REACTON RATE CALCULATION FUNCTION
Function CalcR(T, P, z, VmQty, MwQty)
  '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
  'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  Vml = VmQty.Convert(Vml,"cm3/mol","l/mol")
  '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
      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)
  'Units conversion
  Set VmQty = Repository.QuantityByName("Molar volume")
  Set MwQty = Repository.QuantityByName("Molar mass")
  'Reaction rate
  Rate = CalcR(T, P, z, VmQty, MwQty)
  'Temperature derivative
  dT      = 0.1
  T1      = T + dT
  Rate1   = CalcR(T1, P, z, VmQty, MwQty)
  dRatedT = (Rate1-Rate)/dT
  'Pressure derivative
  dP = 0.1
  P1 = P + dP
  Rate1 = CalcR(T, P1, z, VmQty, MwQty)
  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, VmQty, MwQty)
    dRatedN(i) = (Rate1-Rate)/dz
```



```
  Next
End Sub
```


7. Simulation

7.1. Process description

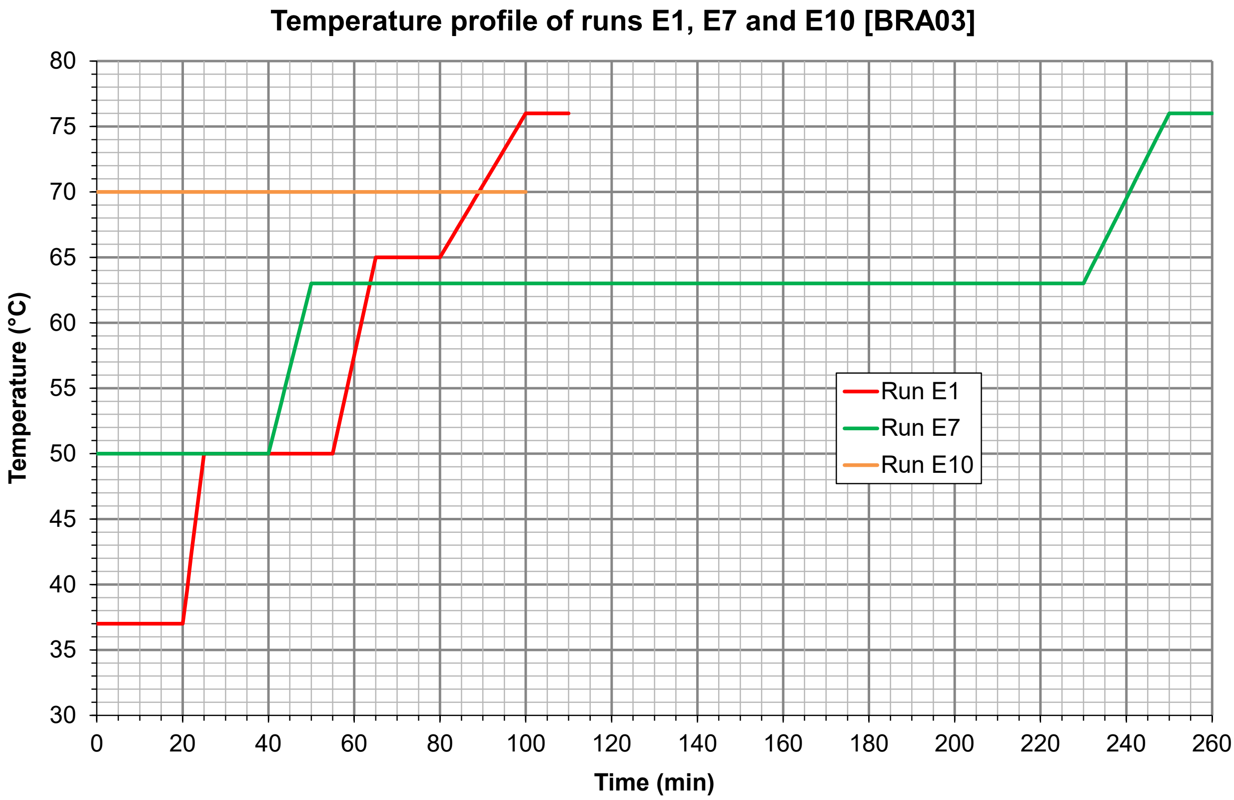
The reactor used for the hydrolysis of starch is a single-phase liquid reactor.

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_{malt} or in U/kg_{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.

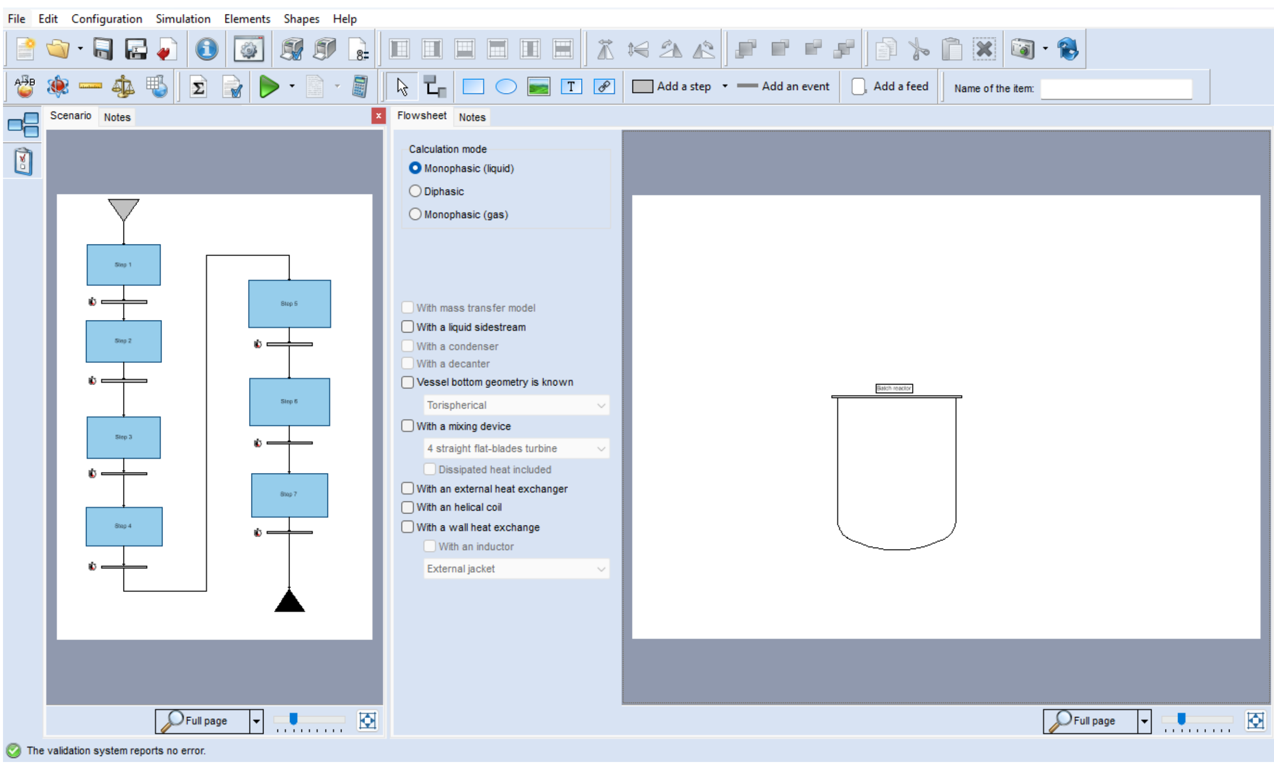
The following table presents the experiments concentration from [BRA03] and the corresponding initial loads used in the simulations.

Initial conditions		
Temperature	37°C	
Pressure	1 atm	
Initial compositions		
	Concentration [BRA03]	**Load (kg)**
Water	-	70
Maltose	5 g/kg_{malt}	0.100
Glucose	4 g/kg_{malt}	0.080
Small grains of non gelatinized starch	113.5 g/kg_{malt}	0.1135
Big grains of non gelatinized starch		2.1565
α sites	210 U/kg_{malt}	4.200
β sites	380 U/kg_{malt}	7.600
Malt	-	20
Other component	0	0

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 reactor temperature" 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.



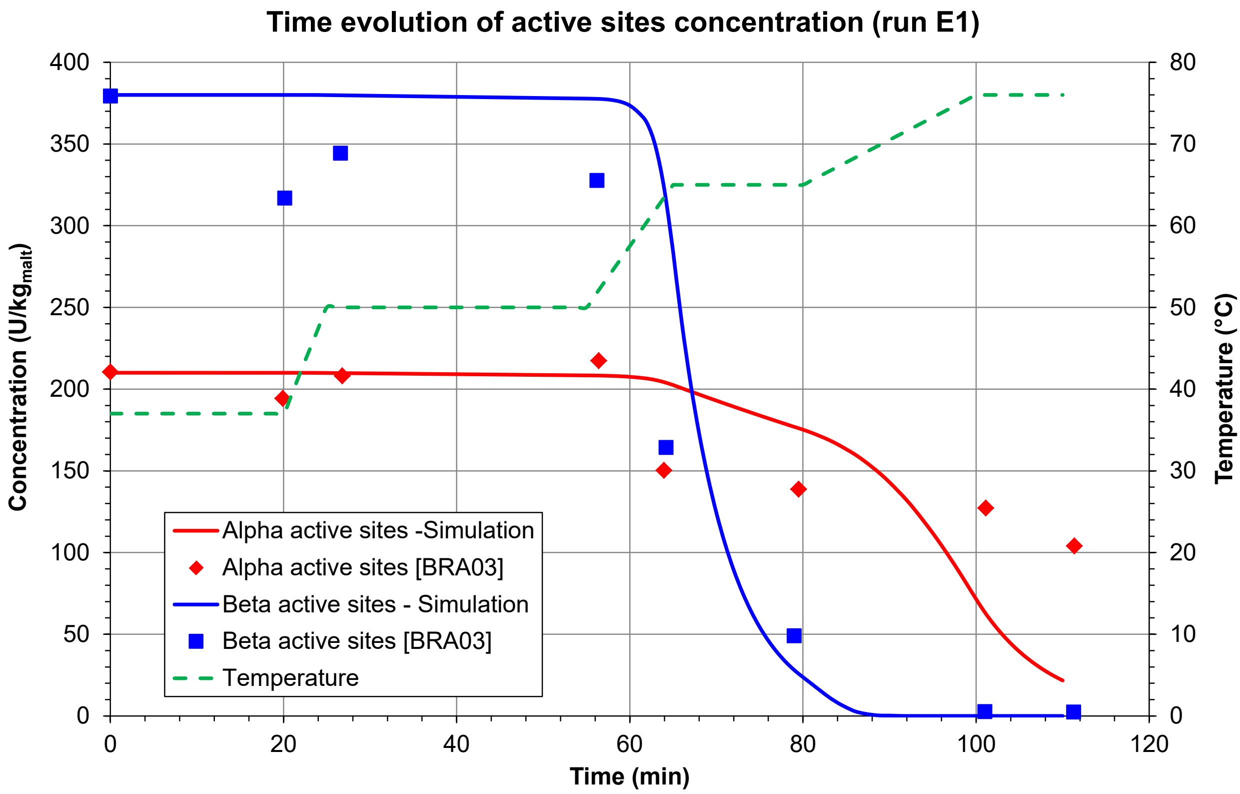
The following screen shot presents the simulation of the Run E1 experiment. The scenario is presented on the left part of this screen shot and the flowsheet on the right part.

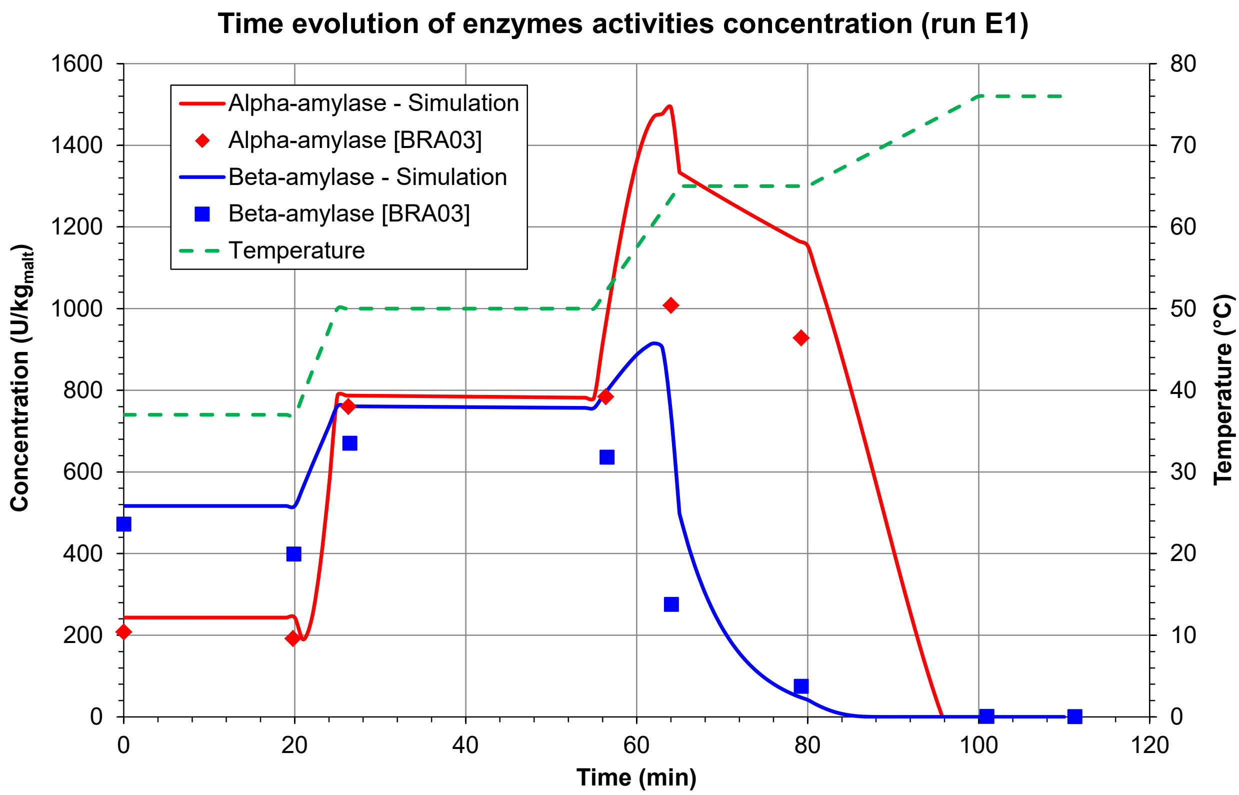


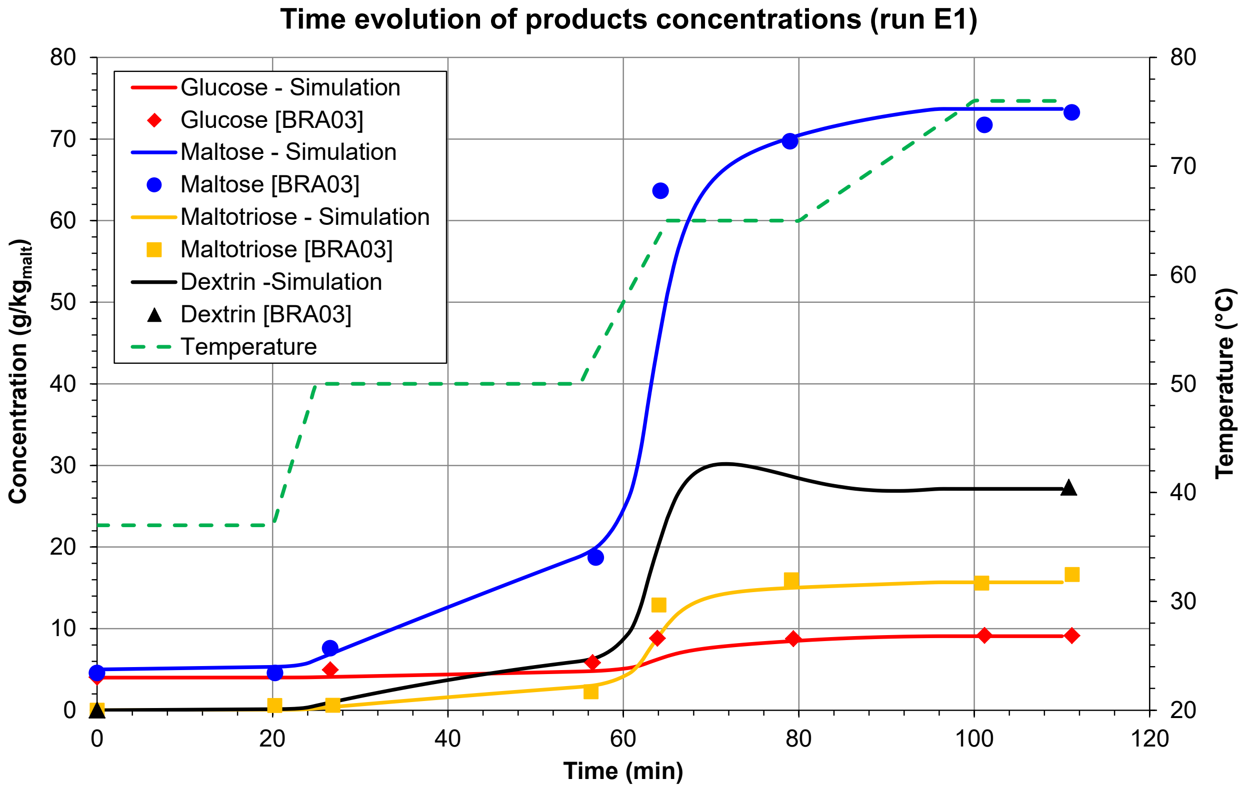
7.2. Results

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

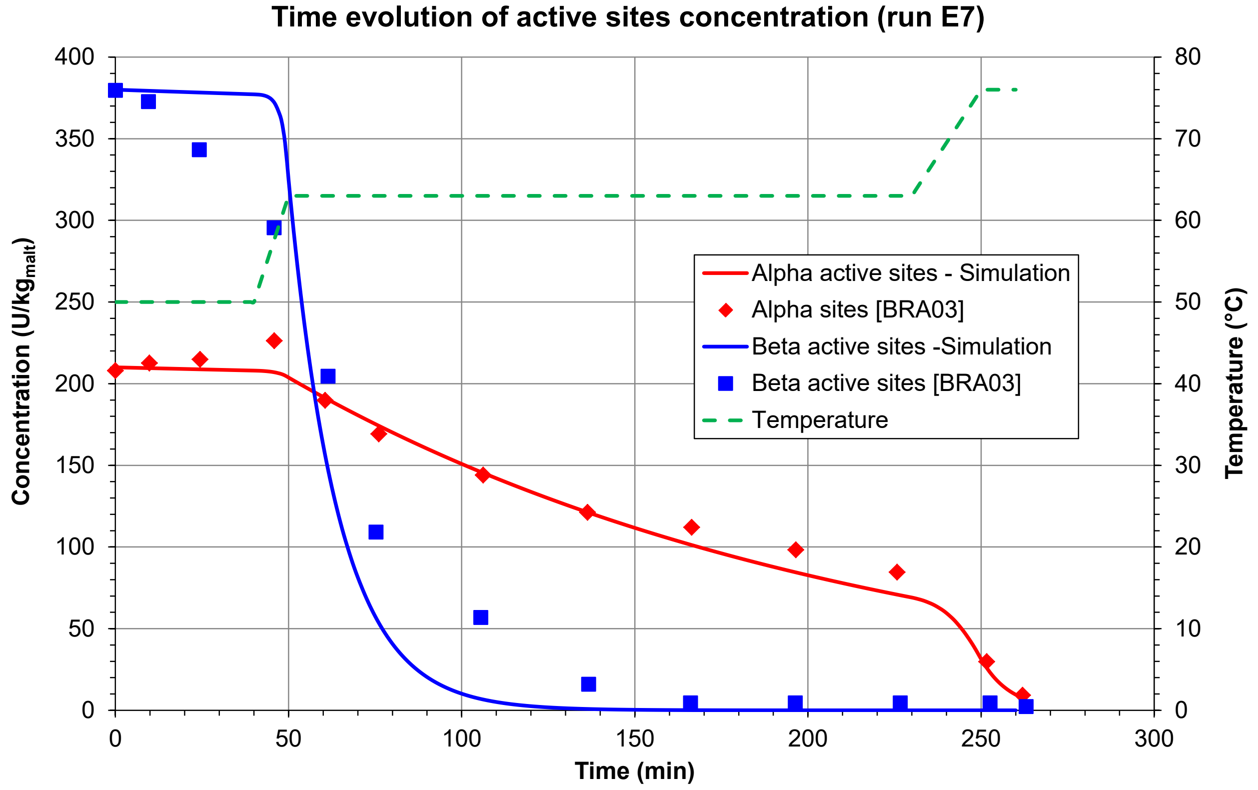
7.2.1. Run E1

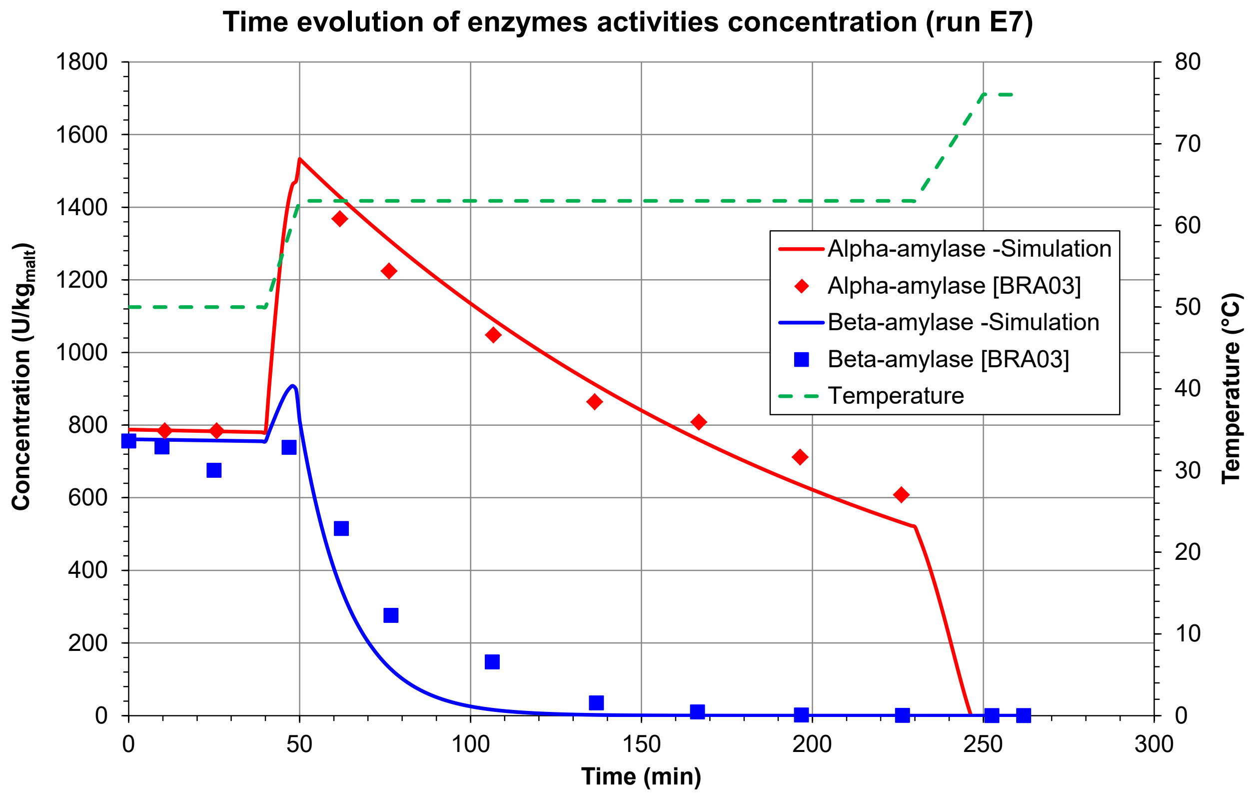


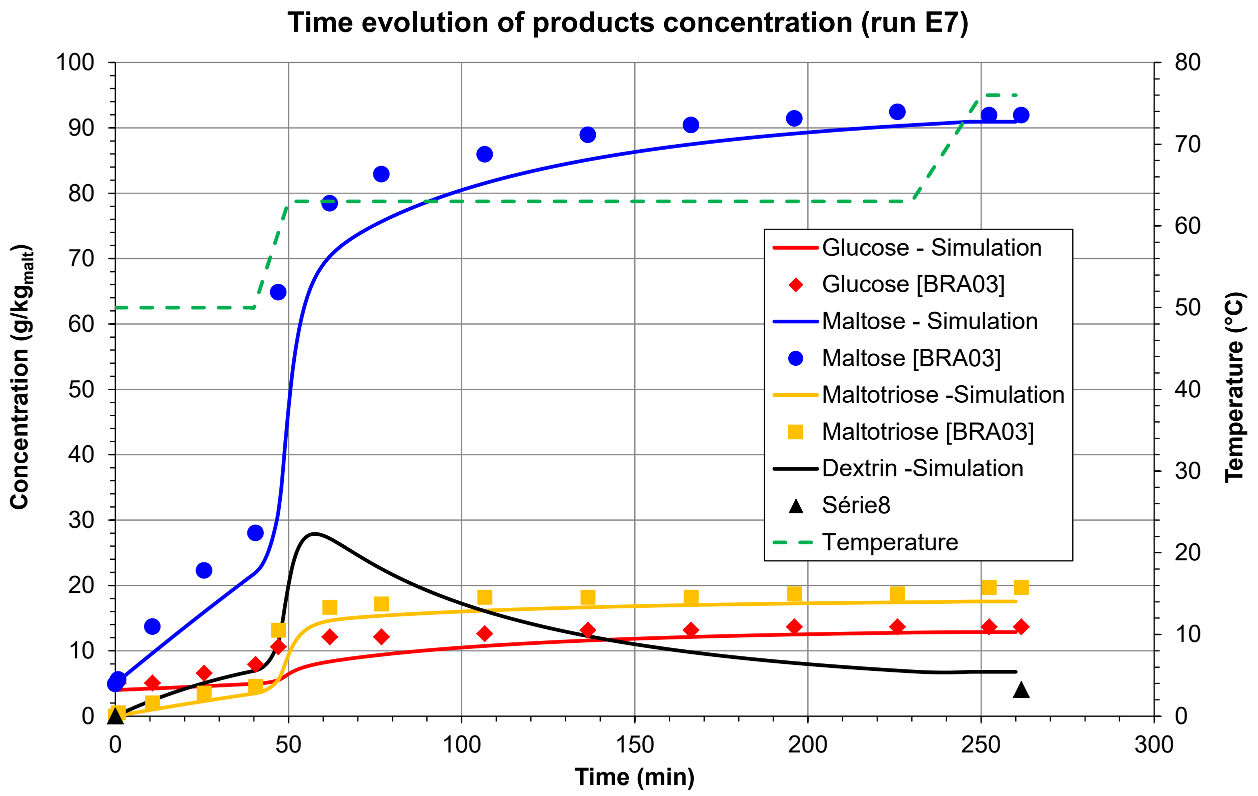



Time evolution of products concentrations (run E1)
Glucose - Simulation
Glucose [BRA03]
Maltose - Simulation
Maltose [BRA03]
Maltotriose - Simulation
Maltotriose [BRA03]
Dextrin -Simulation
Dextrin [BRA03]
Temperature
Concentration (g/kg$_{malt}$)
Temperature (°C)
Time (min)
0
10
20
30
40
50
60
70
80
100
120

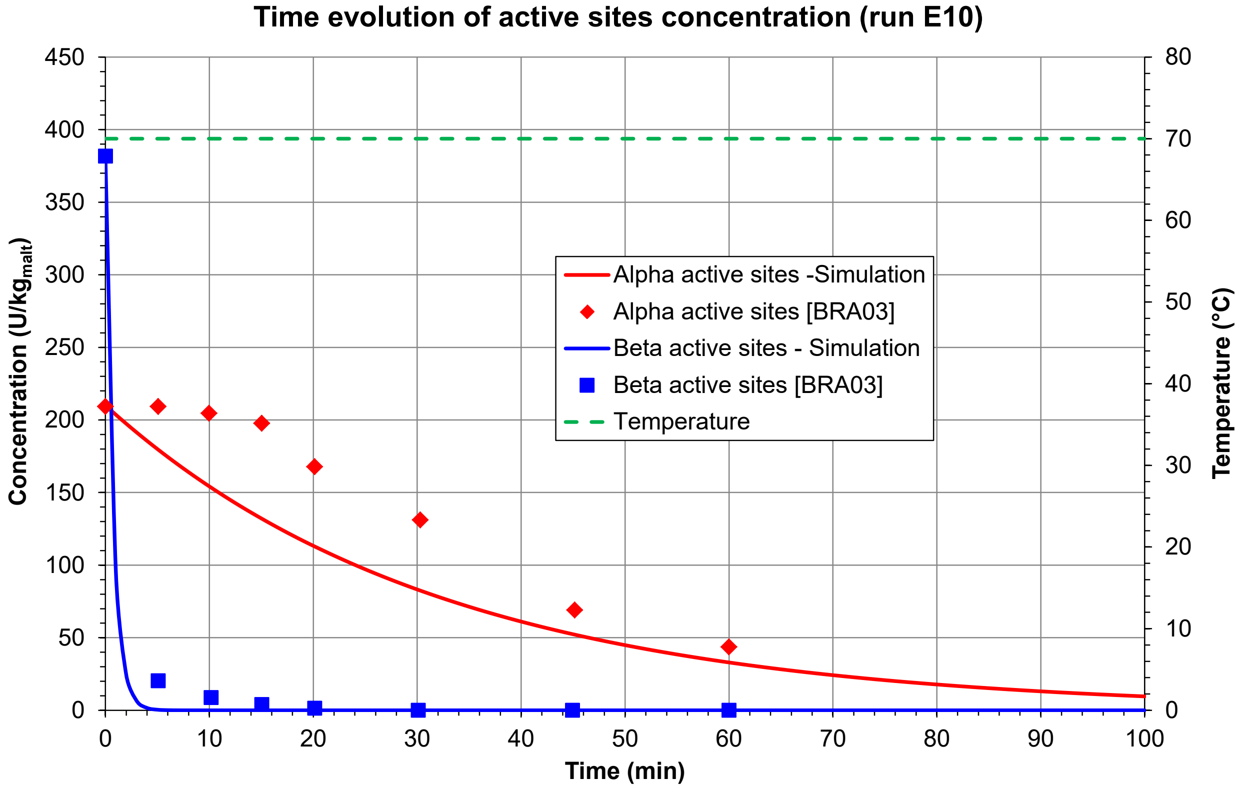
7.2.2. Run E7

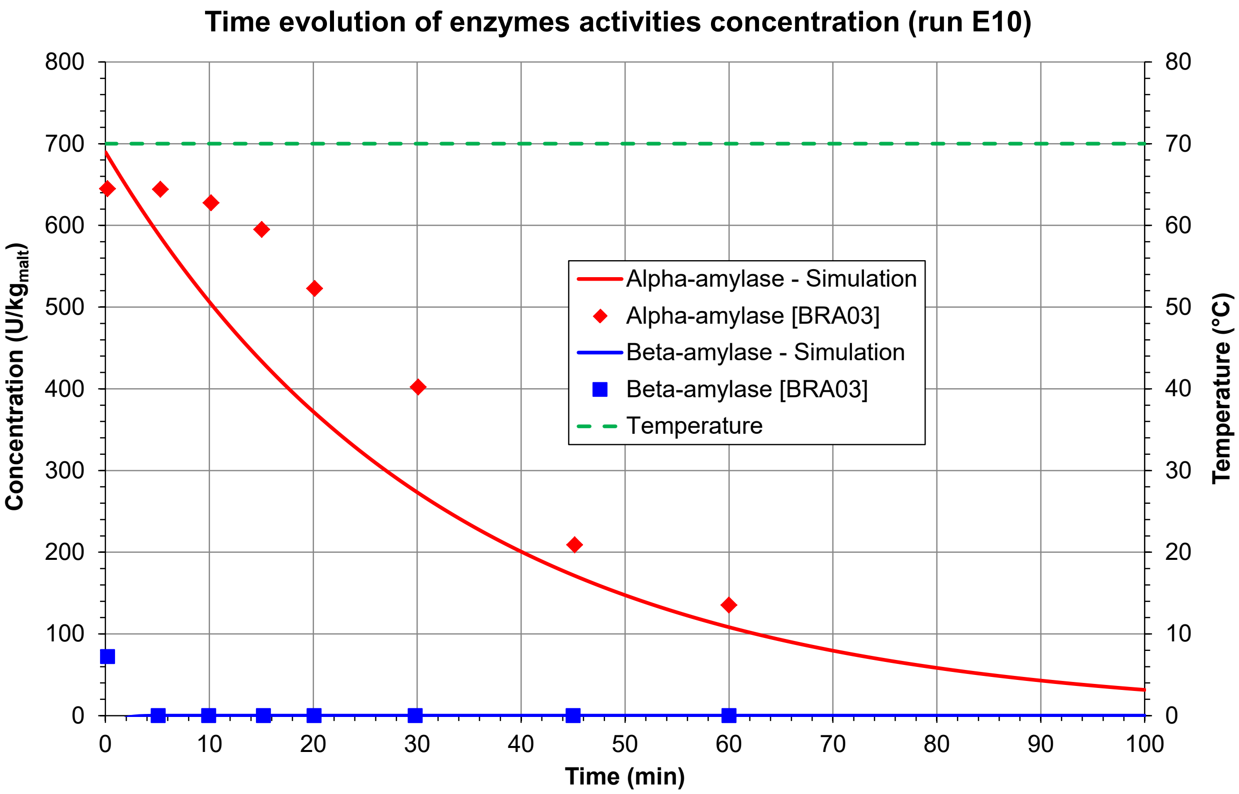

Time evolution of active sites concentration (run E7)
Concentration (U/kgmalt)
Temperature (°C)
Time (min)
Alpha active sites - Simulation
Alpha sites [BRA03]
Beta active sites -Simulation
Beta active sites [BRA03]
Temperature
0
50
100
150
200
250
300
350
400
10
20
30
40
60
70
80

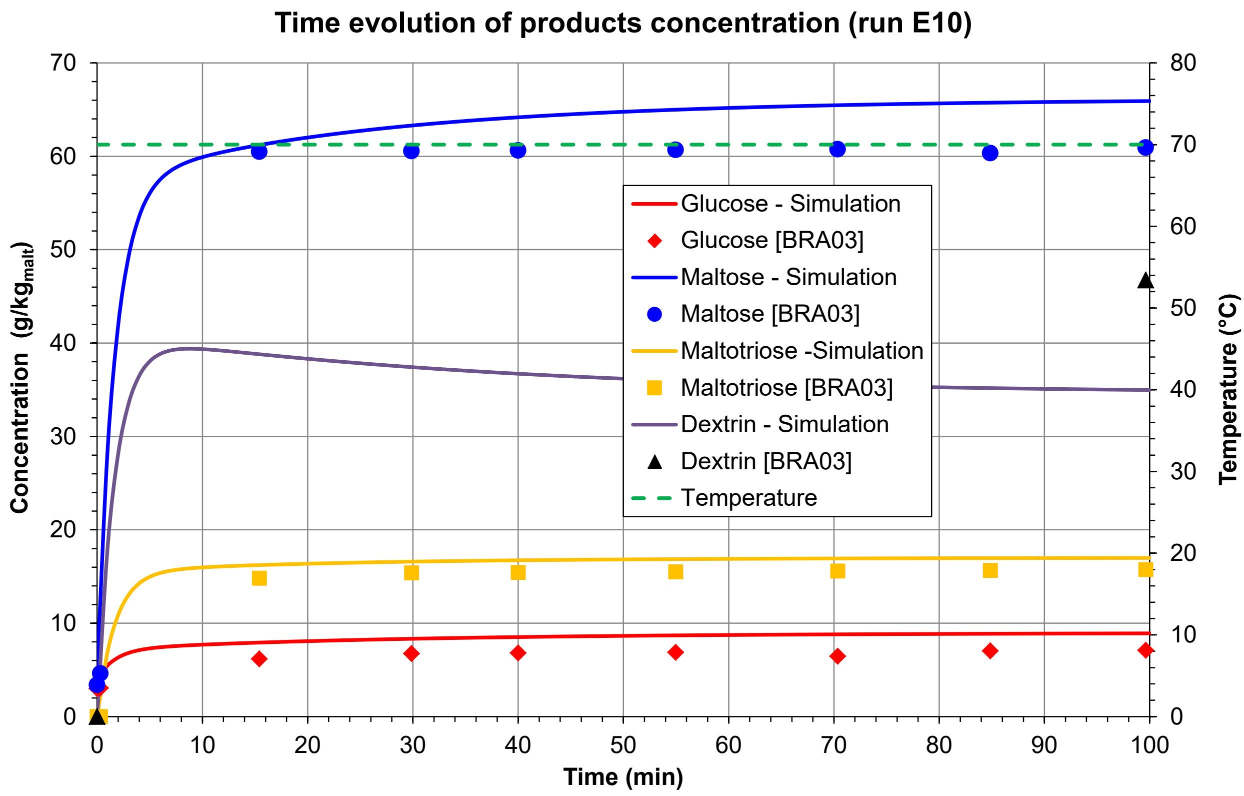

Time evolution of enzymes activities concentration (run E7)
Concentration (U/kgmalt)
Temperature (°C)
Time (min)
Alpha-amylase -Simulation
Alpha-amylase [BRA03]
Beta-amylase -Simulation
Beta-amylase [BRA03]
Temperature
0
200
400
600
800
1000
1200
1400
1600
1800
10
20
30
40
50
60
70
80
100
150
250
300


Time evolution of products concentration (run E7)
Concentration (g/kg$_{malt}$)
Temperature (°C)
Time (min)
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
0
10
20
30
40
50
60
70
80
Glucose - Simulation
Glucose [BRA03]
Maltose - Simulation
Maltose [BRA03]
Maltotriose -Simulation
Maltotriose [BRA03]
Dextrin -Simulation
Série8
Temperature

7.2.3. Run E10


Time evolution of active sites concentration (run E10)
Concentration (U/kg$_{malt}$)
Temperature (°C)
Time (min)
Alpha active sites -Simulation
Alpha active sites [BRA03]
Beta active sites - Simulation
Beta active sites [BRA03]
Temperature
0
50
100
150
200
250
300
350
400
450
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
80


Time evolution of enzymes activities concentration (run E10)
Concentration (U/kg$_{malt}$)
Temperature (°C)
Time (min)
Alpha-amylase - Simulation
Alpha-amylase [BRA03]
Beta-amylase - Simulation
Beta-amylase [BRA03]
Temperature
0
100
200
300
400
500
600
700
800
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
80


Time evolution of products concentration (run E10)
Concentration (g/kgmalt)
Temperature (°C)
Time (min)
Glucose - Simulation
Glucose [BRA03]
Maltose - Simulation
Maltose [BRA03]
Maltotriose -Simulation
Maltotriose [BRA03]
Dextrin - Simulation
Dextrin [BRA03]
Temperature

8. REFERENCES

[BRA03] BRANDAM C., MEYER X.M., PROTH J., STREHAIANO P., PINGAUD H., "An Original Kinetic Model for the Enzymatic Hydrolysis of Starch during Mashing", Biochem. Eng. J., 13, 43-52 (2003)

[ROW2105] ROWLEY R.L., WILDING W.V., OSCARSON J.L., GILES N.F., "DIPPR® Data Compilation of Pure Chemical Properties", Design Institute for Physical Properties, AIChE, New York, NY (2015)

[WIK15] https://en.wikipedia.org/wiki/Starch (link verify in September 2015)

9. Nomenclature

a_α	Global activity of α-amylase enzyme	U/kg_{malt}
a_β	Global activity of β-amylase enzyme	U/kg_{malt}
a_S	Relative specific enzyme activity	(-)
$[D]$	Dextrin concentration	g/kg_{malt}
$[E_\alpha]$	Active α-amylase enzyme site concentration	g/kg_{malt}
$[E_\beta]$	Active β-amylase enzyme site concentration	g/kg_{malt}
E_i	Activation energy	J/mol
$k_{\alpha,mal}$	Kinetic factor	kg/(U.s)
$k'_{\alpha,mal}$	Kinetic factor	kg/(U.s)
$k_{\beta,mal}$	Kinetic factor	kg/(U.s)
$k'_{\beta,mal}$	Kinetic factor	kg/(U.s)
$k_{d\alpha}$	Pre-exponential factor	s^{-1}
$k_{d\beta}$	Pre-exponential factor	s^{-1}
k_{dex}	Kinetic factor	kg/(U.s)
k_{g1}	Pre-exponential factor	s^{-1}
k_{g2}	Pre-exponential factor	s^{-1}
k_{gl}	Kinetic factor	kg/(U.s)
k'_{gl}	Kinetic factor	kg/(U.s)
k_{mlt}	Kinetic factor	kg/(U.s)
k'_{mlt}	Kinetic factor	kg/(U.s)
k_{sg}	Pre-exponential factor	s^{-1}
R	Perfect gas constant	J/(mol/K)
$r_{d\alpha}$	Rate of reaction	U/(kg.s)
$r_{d\beta}$	Rate of reaction	U/(kg.s)
r_{dex}	Rate of reaction	$g/(kg_{malt}.s)$
r_g	Rate of reaction	$g/(kg_{malt}.s)$

r_{gl}	Rate of reaction	$g/(kg_{malt}.s)$
r'_{gl}	Rate of reaction	$g/(kg_{malt}.s)$
r_{mal}	Rate of reaction	$g/(kg_{malt}.s)$
r'_{mal}	Rate of reaction	$g/(kg_{malt}.s)$
r_{mlt}	Rate of reaction	$g/(kg_{malt}.s)$
r'_{mlt}	Rate of reaction	$g/(kg_{malt}.s)$
r_{sg}	Rate of reaction	$g/(kg_{malt}.s)$
$[S_g]$	Gelatinized starch concentration	g/kg_{malt}
$[S_S]$	Big non gelatinized starch grains concentration	g/kg_{malt}
$[S_{SS}]$	Small non gelatinized starch grains concentration	g/kg_{malt}
T	Temperature	K
T_g	Threshold temperature	°C