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BATCHREACTOR APPLICATION EXAMPLE

AGRI-FOOD INDUSTRY

SIMULATION OF BATCH TOMATO SAUCE OXIDATION

EXAMPLE PURPOSE
This example illustrates how to model a bioreactor, taking into account bioreaction kinetics as well as mass transfer resistance in the liquid phase. This agri-food processing example deals with the reactions taking place during the production of tomato sauce between components such as ascorbic acid, chlorogenic acid and β-carotene. The studied reactions involve the oxidation and degradation of the first compound, the oxidation of the second one and the isomerization of the third one. The bioreaction kinetics are modeled using the advanced mode available in Simulis Reactions, the chemical reactions server of BatchReactor software. This feature enables the user to code custom mathematical models that are not included in standard kinetic model libraries. The oxygen transfer in the liquid phase is an essential step that has a major influence on the oxidation reactions yields. Consequently, the “mass transfer model” option is activated and enables to account for the mass transfer resistance and rigorously compute the oxygen concentration in the liquid phase.

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CORRESPONDING BATCHREACTOR FILES	*BATCHREA_EX_EN - Tomato sauce Run 050C.pbpr* *BATCHREA_EX_EN - Tomato sauce Run 070C.pbpr* *BATCHREA_EX_EN - Tomato sauce Run 095C.pbpr* *BATCHREA_EX_EN - Tomato sauce Run 105C.pbpr*

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1. INTRODUCTION

This example presents the study of the reactions that occur during the production of tomato sauce when transforming fresh tomatoes into concentrated sauce.

Four main reactions are analyzed:

- the ascorbic acid oxidation,
- the ascorbic acid degradation,
- the chlorogenic acid oxidation,
- the β-carotene isomerization,

Regarding the oxidations, the ascorbic acid reacts with oxygen to produce dehydroascorbic acid and hydrogen peroxide, while chlorogenic acid reacts with oxygen to produce quinone and hydrogen peroxide. It has been observed that these two reactions are limited by the oxygen transfer to the liquid phase. Consequently, the mass transfer resistance is taken into account in the model. In the isomerization, the reactant is the E-carotene (trans-isomer) which reacts to form Z-carotene (cis-isomer). Finally, for the degradation of the ascorbic acid it is considered that one molecule of this compound gives one molecule of degraded ascorbic acid.

All reactions are assumed to follow the Arrhenius law and the values for the activation energy and the pre-exponential factor were taken from [BRA12]. These parameters depend on the temperature range.

2. REACTION MECHANISM

The reactions taken into account during the transformation of fresh tomatoes into concentrated sauce are the following ones:

- ✓ Chlorogenic acid oxidation:

$$Chlorogenic\ acid + Oxygen \longrightarrow Chlorogenic\ acid\ quinone + Hydrogen\ peroxide$$

Namely,

$$C_{16}H_{18}O_9 + O_2 \longrightarrow C_{16}H_{16}O_9 + H_2O_2 \quad \text{(R1)}$$

- ✓ Ascorbic acid oxidation:

$$Ascorbic\ acid + Oxygen \longrightarrow Dehydroascorbic\ acid + Hydrogen\ peroxide$$

Namely,

$$C_6H_8O_6 + O_2 \longrightarrow C_6H_6O_6 + H_2O_2 \quad \text{(R2)}$$

- ✓ Ascorbic acid thermal degradation:

$$Ascorbic\ acid \longrightarrow Degraded\ ascorbic\ acid$$

Namely,

$$C_6H_8O_6 \longrightarrow C_6H_8O_{6\,(degraded)} \quad \text{(R3)}$$

- ✓ β-carotene isomerization:

$$E\text{---}carotene \longrightarrow Z\text{---}carotene$$

Namely,

$$C_{40}H_{56\,(trans)} \longrightarrow C_{40}H_{56\,(cis)} \quad \text{(R4)}$$

3. COMPONENTS

The following components are taken into account in the simulation:

Name	CAS number[1]
Oxygen (*)	7782-44-7
Nitrogen (*)	7727-37-9
Water (*)	7732-18-5
Hydrogen peroxide(*)	7722-84-1
Ascorbic acid(*)	50-81-7
Degraded ascorbic acid(*)	
Dehydroascorbic acid	
Chlorogenic acid	
Chlorogenic acid quinone	
E-carotene	
Z-carotene	
Dry matter	

Compounds with an asterisk are taken from the standard database of Simulis Thermodynamics (thermodynamic calculation server used in BatchReactor). The thermophysical properties stored in this database are the DIPPR recommended values [ROW21].

For the compounds “Oxygen” and “Nitrogen”, the parameters of the vapor pressure correlation were replaced by the Henry’s law parameters, allowing to better compute the solubility of these gases in the liquid phase.

$$Ln(P^0) = A + \frac{B}{T} + C \times ln(T) + D \times T^E \quad \text{(Equation 101)}$$

Coefficient	Oxygen	Nitrogen
T_{min}	273 K	63.15 K
T_{max}	617 K	600 K
A	151.011089	152.79
B	-6889.6	-6921.99
C	-18.554	-18.7292
D, E	0	0

The “degraded ascorbic acid” compound is a clone of the ascorbic acid compound. Only the CAS number[1] has been changed (arbitrary number).

[1] *CAS Registry Numbers® are the intellectual property of the American Chemical Society; and are used by ProSim SA with the express permission of ACS. CAS Registry Numbers have not been verified by ACS and may be inaccurate.*

The other compounds (dehydroascorbic acid, chlorogenic acid, chlorogenic acid quinone, E-carotene, Z-carotene and dry matter) were created using the function “Create a new compound” of Simulis Thermodynamics. Their properties are provided below:

- ✓ CAS number[1] : Arbitrary number
- ✓ Chemical formula : From literature
- ✓ Molecular weight : From literature
- ✓ 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

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

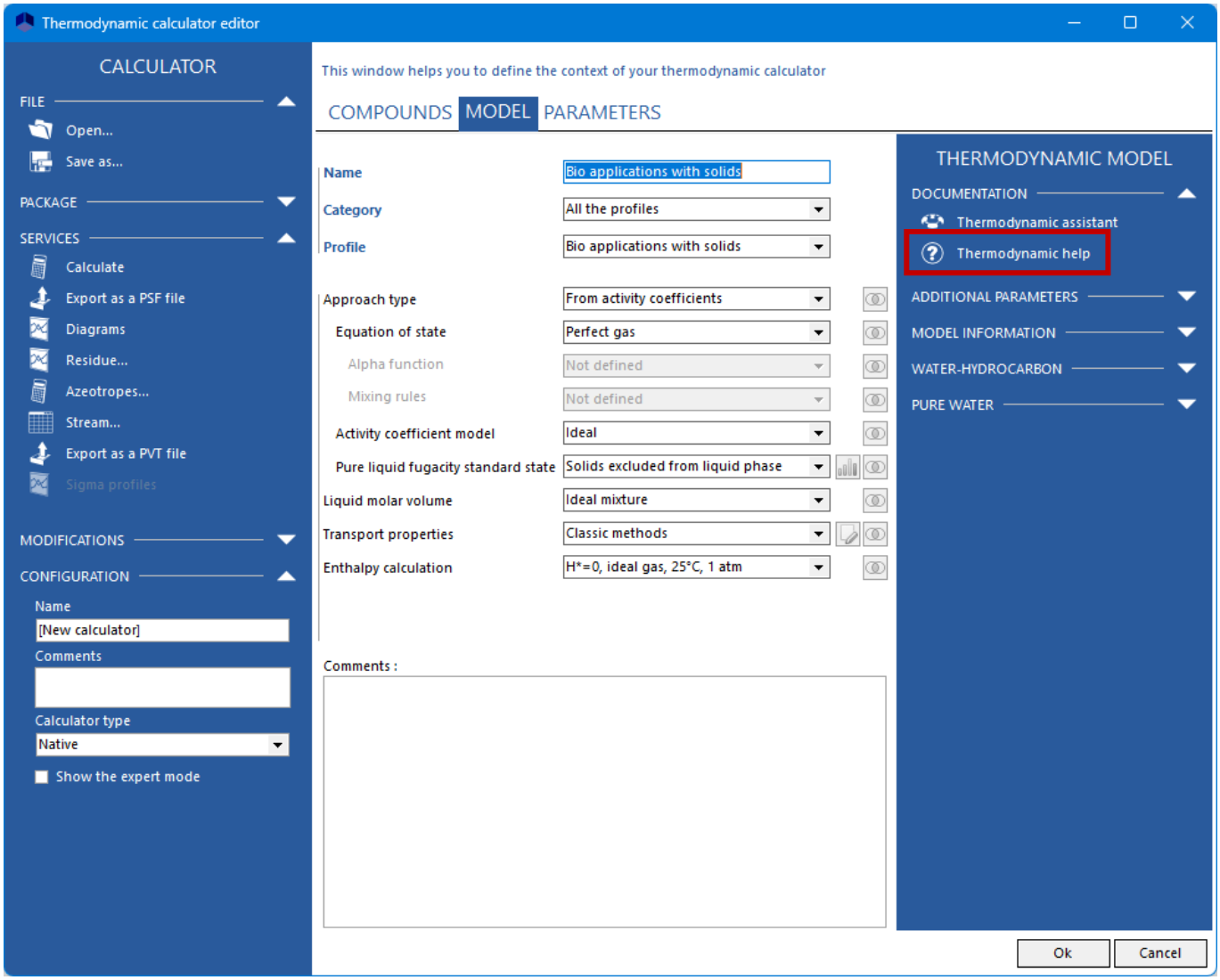
- ✓ Vaporization enthalpy : 0 J/mol
- ✓ Liquid density : Same as water

All of the experimental data are based on the dry matter quantity in the system, consequently the dry matter compound was created. A molecular weight of 1 g/mol is adopted. This compound is considered as an insoluble solid.

4. THERMODYNAMIC MODEL

Reactions occur at temperatures up to 105°C and atmospheric pressure, so the gas phase is modeled using the ideal gas law.

The liquid phase contains an insoluble solid, the dry matter. This solid has been represented as a non-volatile liquid (see § 3) which must be excluded from the liquid phase for the vapor-liquid equilibrium calculations. Otherwise, it would modify the real composition of the liquid phase along with the vapor-liquid equilibrium constant of the volatile components. Therefore, the thermodynamic profile “Bio applications with solids” has been selected, for which the “Solids excluded from liquid phase” model is defined to calculate the liquid fugacity. More detailed information is available in the thermodynamic help file:



5. MASS TRANSFER MODEL

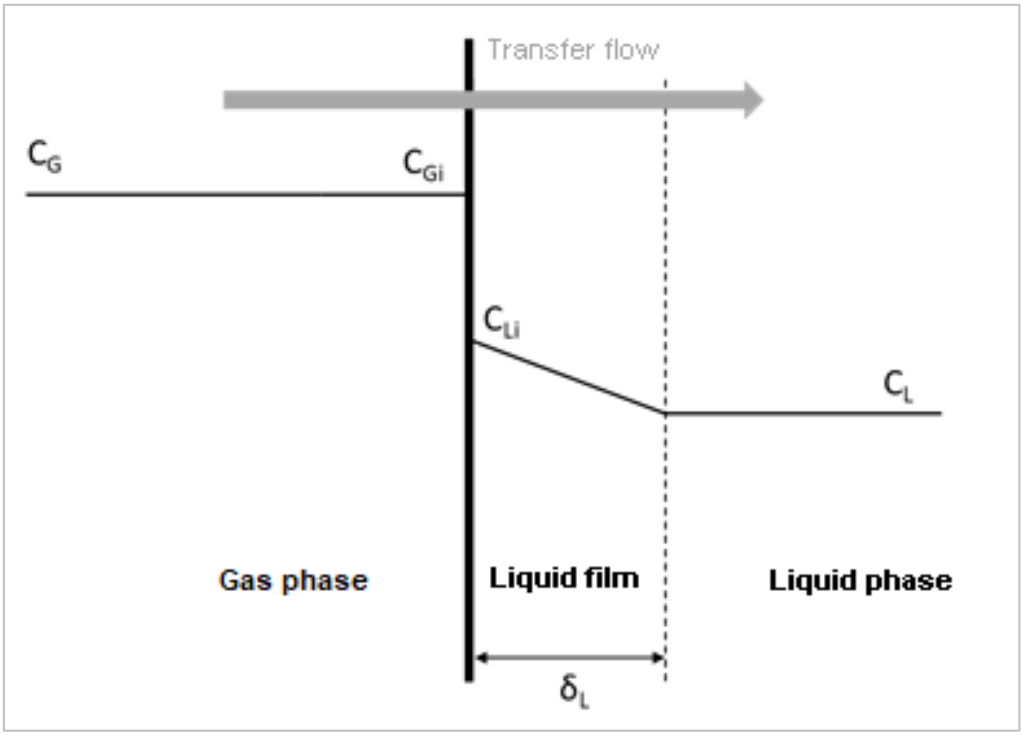
5.1. Model description

The mass transfer model is activated in order to account for the mass transfer resistance of oxygen in the liquid phase. This model is based on the two-film theory. According to this theory, on either side of the gas-liquid interface, there is a film in which mass transfer is governed by diffusion. Assuming that the mass transfer resistance is mostly localized on the liquid side, the gas phase is considered at the thermodynamic equilibrium with the liquid film, and the mass transfer flow is calculated from the knowledge of mass transfer coefficients ($k_L a$) in the liquid phase:

$$\Phi = k_L a \, (C_{Li} - C_L)$$

With:

Φ	Mass transfer flow	mol/(L.h)
$k_L a$	Volumetric mass transfer coefficient in the liquid phase	h^{-1}
C	Molar concentration	mol/L

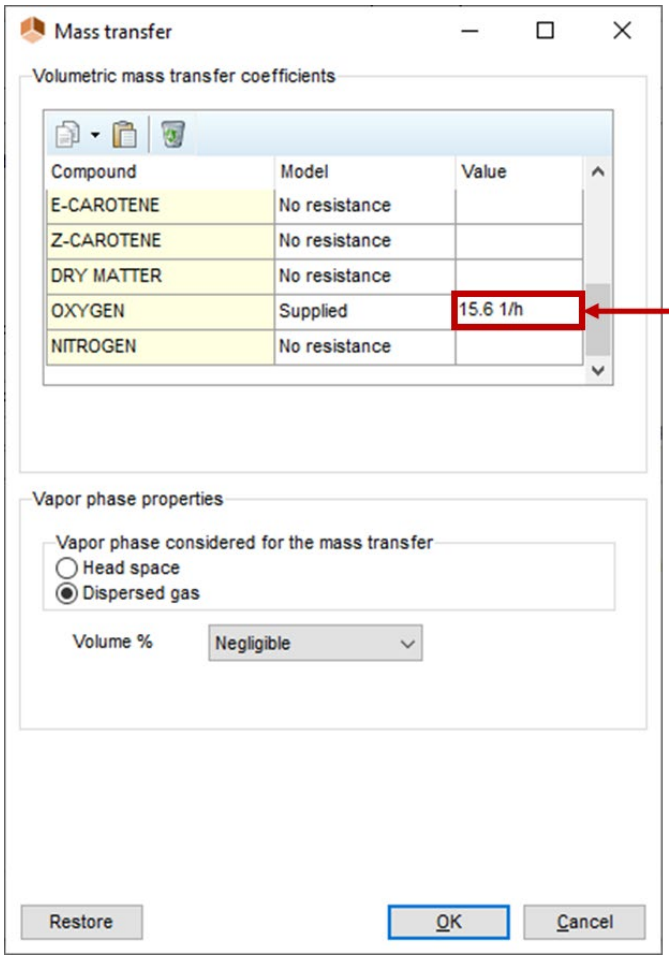


The oxygen mass transfer coefficients in the liquid phase were estimated by [BRA12]:

Temperature	$k_L a$
50°C	15.6 h^{-1}
70°C	38.4 h^{-1}
95°C	105.6 h^{-1}
105°C	151.8 h^{-1}

5.2. Configuration of the mass transfer model in BatchReactor

The “mass transfer model” option is selected form the control panel. Then, the mass transfer model parameters are provided as follows in the “Process” tab:



Enter the value for the oxygen k_La (depends on the operating temperature)

The “dispersed gas” phase (corresponding to the bubbles of gas dispersed in the liquid phase) is considered for the mass transfer. More detailed information is available in the help file (accessible by pressing “F1” from the mass transfer configuration window).

6. REACTION MATHEMATICAL MODEL

6.1. Model description

[BRA12] developed a mathematical model for the reactions taking place during the production of tomato sauce (transformation of fresh tomatoes into concentrated sauce).

- ✓ Rate of the chlorogenic acid oxidation:

$$r_{ACHL} = k^0_{ACHL} \times \exp\left(\frac{-Ea_{ACHL}}{RT}\right) \times [ACHL] \quad \text{(R1)}$$

- ✓ Rate of the ascorbic acid oxidation:

$$r_{AASC} = k^0_{AASC} \times \exp\left(\frac{-Ea_{AASC}}{RT}\right) \times [AASC] \times [O_2] \quad \text{(R2)}$$

- ✓ Rate of the ascorbic acid degradation:

$$r_{AASC(degrad.)} = k^0_{AASC\ (degrad.)} \times \exp\left(\frac{-A_{AASC\ (degrad.)}}{T}\right) \times [AASC] \quad \text{(R3)}$$

- ✓ Rate of β-carotene isomerization:

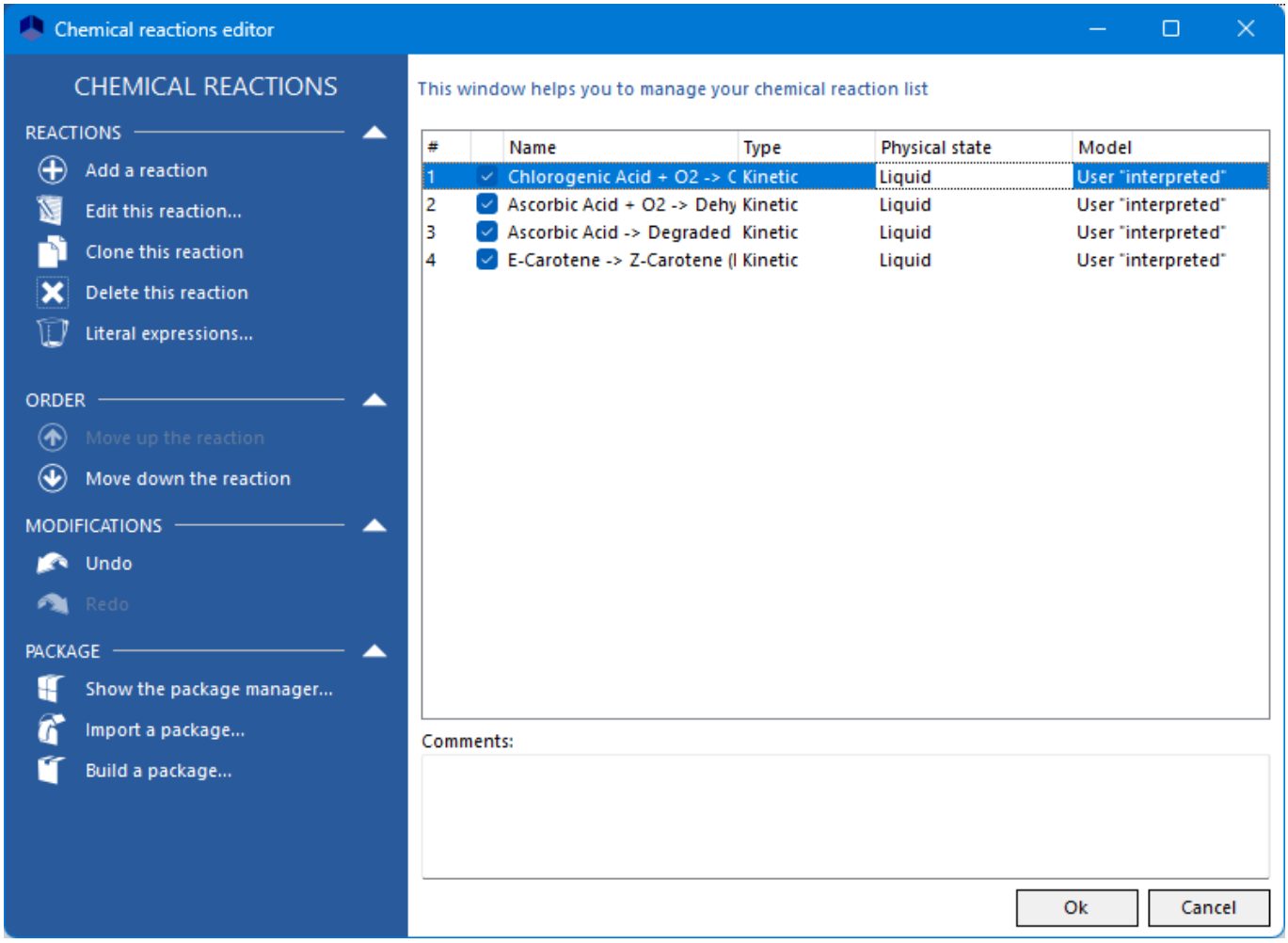
$$r_{Caro} = k^0_{Caro} \times \exp\left(\frac{-Ea_{Caro}}{RT}\right) \times [E\text{-}Carotene] \quad \text{(R4)}$$

All parameters taken from [BRA12] are presented in the following table. Outside from the indicated temperature ranges, it is assumed that the corresponding reactions do not occur (the reaction rate is null):

Compound	Temperature range	Parameters
Chlorogenic acid (ACHL)	25°C – 95°C	$k^0_{ACHL} = 5180\ min^{-1}$ $Ea_{ACHL} = 35100\ J.mol^{-1}$
Ascorbic acid (AASC)	25°C – 95°C	$k^0_{AASC} = 12300\ min^{-1}.100 g/mg$ $Ea_{AASC} = 37400\ J.mol^{-1}$
	25°C – 125°C	$k^0_{AASC\ (degrad.)} = 1{,}75e6\ min^{-1}$ $A_{AASC\ (degrad.)} = 7480\ K$
β-Carotene (Caro)	95°C – 125°C	$k^0_{Caro} = 2070\ min^{-1}$ $Ea_{Caro} = 39300\ J.mol^{-1}$

6.2. Configuration of the kinetic model using Simulis Reactions

The four reactions were described in Simulis Reactions:



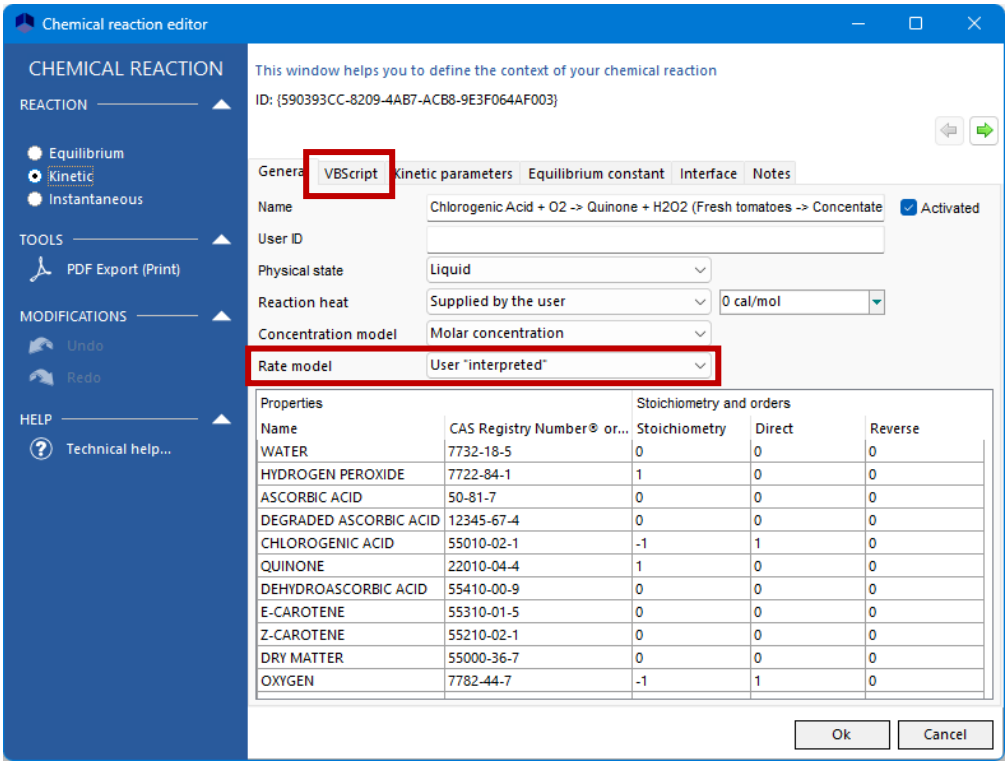
As the kinetic parameters of the reactions change according to the temperature range, user “interpreted” kinetic rate model was used to implement the mathematical models provided by [BRA12], as shown on the next pages. Thanks to this functionality of Simulis Reactions, user can write his own code for the kinetic models using VBScript (Microsoft Visual Basic Scripting Edition), which is an interpreted language (*i.e.*, it does not require compilation step 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:

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

' CALCULATION PROCEDURE
' --- Data ---
' 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)
  'Model parameters
  R  = 8.31              '(J/mol.K)
  K0 = 5.18E3/60         '(s-1)
  Ea = 35100             '(J/mol)
```

```
  K  = K0*exp(-Ea/(R*T)) '(s-1)


'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  'Units conversion
  Set Quantity   = Repository.QuantityByName("Molar volume")
  Vml            = Quantity.Convert(Vml,"cm3/mol","l/mol")
  Set MwQty      = Repository.QuantityByName("Molar mass")
  'Calculation of the concentrations
  CASN_ChloroAcid = "55010-02-1"
  For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
      If (.CasRegistryNumber = CASN_ChloroAcid) Then
          ipos_ChloroAcid = i-1
          Mw_ChloroAcid   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
          C_ChloroAcid    = z(ipos_ChloroAcid)*Mw_ChloroAcid/Vml
      End If
    End With
  Next
  'Calculation of the rate of the reaction
  If (T >= 298.1 And T <= 368.2) Then 'Temperature between 25°C and 95°C
      Rate = K*C_ChloroAcid           '(g/L.s)
      Rate = Rate/Mw_ChloroAcid       '(mol/L.s)
  Else
      Rate = 0
  End If
End Sub
```

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

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


' CALCULATION PROCEDURE
' --- Data ---
' 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)
  'Model parameters
  R  = 8.31              '(J/mol.K)
  K0 = 12.3E3/60         '(s-1.100g/mg)
  Ea = 37400             '(J/mol)
  K  = K0*exp(-Ea/(R*T)) '(s-1)

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

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

  'Calculation of the concentrations
  CASN_Oxygen = "7782-44-7"
  For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
      If (.CasRegistryNumber = CASN_Oxygen) Then
          ipos_Oxygen = i-1
          Mw_Oxygen   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
          C_Oxygen    = z(ipos_Oxygen)*Mw_Oxygen/Vml
      End If
    End With
  Next

  CASN_AscorbicAcid = "50-81-7"
  For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
      If (.CasRegistryNumber = CASN_AscorbicAcid) Then
          ipos_AscorbicAcid = i-1
          Mw_AscorbicAcid   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
          C_AscorbicAcid    = z(ipos_AscorbicAcid)*Mw_AscorbicAcid/Vml
      End If
    End With
  Next
```

```
  'Calculation of the reaction rate
  C_Oxygen = C_Oxygen*100             '(mg/100g)
  K = K*C_Oxygen
  If (T >= 298.1 And T <= 368.2) Then 'Temperature between 25°C and 95°C
      Rate = K*C_AscorbicAcid        '(g/L.s)
      Rate = Rate/Mw_AscorbicAcid    '(mol/L.s)
  Else
      Rate = 0
  End If
End Sub
```

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

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


' CALCULATION PROCEDURE
' --- Data ---
' 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)
  'Model parameters
  R  = 8.31        '(J/mol.K)
  K0 = 1.75E6/60   '(s-1)
  A  = 7.48E3      '(K)
  K = K0*exp(-A/T) '(s-1)
  'Calculation of the molar volume
  Vml = ThermoCalculator.PCalcVml(T,P,z)
  'Units conversion
  Set Quantity   = Repository.QuantityByName("Molar volume")
  Vml            = Quantity.Convert(Vml,"cm3/mol","l/mol")
  Set MwQty      = Repository.QuantityByName("Molar mass")
  'Calculation of the concentrations
```



```
  CASN_AscorbicAcid = "50-81-7"
  For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
      If (.CasRegistryNumber = CASN_AscorbicAcid) Then
          ipos_AscorbicAcid = i-1
          Mw_AscorbicAcid   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
          C_AscorbicAcid    = z(ipos_AscorbicAcid)*Mw_AscorbicAcid/Vml
      End If
    End With
  Next
  'Calculation of the reaction rate
  If (T >= 298.1 And T <= 398.2) Then 'Temperature between 25°C and 125°C
      Rate = K*C_AscorbicAcid        '(g/L.s)
      Rate = Rate/Mw_AscorbicAcid    '(mol/L.s)
  Else
      Rate = 0
  End If
End Sub
```

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

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


' CALCULATION PROCEDURE
' --- Data ---
' 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)
  'Model parameters
  R  = 8.31              '(J/mol.K)
  K0 = 2.07E3/60         '(s-1)
  Ea = 39300             '(J/mol)
```

```
  K  = K0*exp(-Ea/(R*T)) '(s-1)
  'Calculation of the molar volume
  Vml=ThermoCalculator.PCalcVml(T,P,z)
  'Units conversion
  Set Quantity   = Repository.QuantityByName("Molar volume")
  Vml            =  Quantity.Convert(Vml,"cm3/mol","l/mol")
  Set MwQty      = Repository.QuantityByName("Molar mass")
  'Calculation of the concentrations
  CASN_ECarotene = "55310-01-5"
  For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
      If (.CasRegistryNumber = CASN_ECarotene) Then
          ipos_ECarotene = i-1
          Mw_ECarotene   = MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")
          C_ECarotene    = z(ipos_ECarotene)*Mw_ECarotene/Vml
      End If
    End With
  Next
  'Calculation of the reaction rate
  If (T >= 368.1 And T <= 398.2) Then 'Temperature between 95°C and 125°C
      Rate = K*C_ECarotene            '(g/L.s)
      Rate = Rate/Mw_ECarotene        '(mol/L.s)
  Else
      Rate = 0
  End If
End Sub
```

7. SIMULATION

7.1. Process description

The characteristics of the reactor used for this process are given in the following table.

Reactor	
Type	Closed vapor-liquid
Global volume (vapor + liquid)	500 l
Head space type	Air

The initial conditions are presented in the following table. For the case where T = 105°C, an operating pressure of 1.3 atm was chosen to avoid water evaporation from the solution. A mass of 10 kg of dry matter is chosen and all the other compounds initial loads are calculated according to this quantity. It is assumed that the dry matter represents approximately 5 wt.% of the initial load. Thus, the initial load of water equals 200 kg. Since the head space is initially filled with air, the model calculates the initial concentrations of oxygen and nitrogen in the liquid phase, corresponding to their solubilities for the given operating conditions.

	Experimental conditions [BRA12]				**Simulation initial conditions**			
Temperature	50°C	70°C	95°C	105°C	50°C	70°C	95°C	105°C
Pressure	Not specified				1 atm			1.3 atm
	Experimental concentration [BRA12] ($mg/100g_{dry\ matter}$)				**Simulation initial loads**			
Water	Not specified				200 kg			
Dry matter	Not specified				10 kg			
Chlorogenic acid	8.88	Not specified			0.888 g			
Ascorbic acid	282	338	271	247	28.2 g	33.8 g	27.1 g	24.7 g
E-carotene	Not specified		4.24	Not specified	0.424 g			
Other compounds	0				0 g			

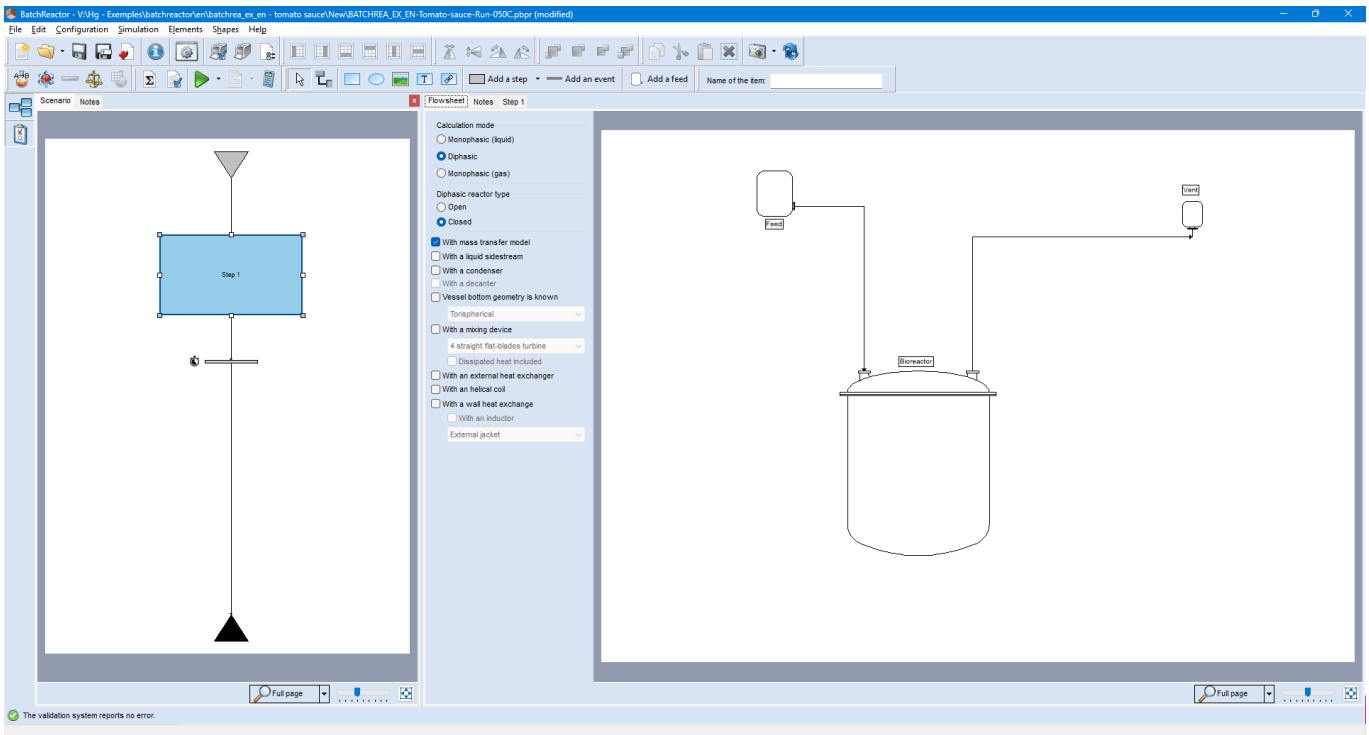
An air stream continuously feeds the reactor in order to make sure that oxygen is kept in excess in the gas phase The characteristics of this stream are:

Temperature	50°C	70°C	95°C	105°C
Pressure	1 atm			1.3 atm
Total flow rate	10 kg/h			
Mole fractions				
Oxygen	0.21			
Nitrogen	0.79			

The operating scenario consists of one isothermal step with the following parameters:

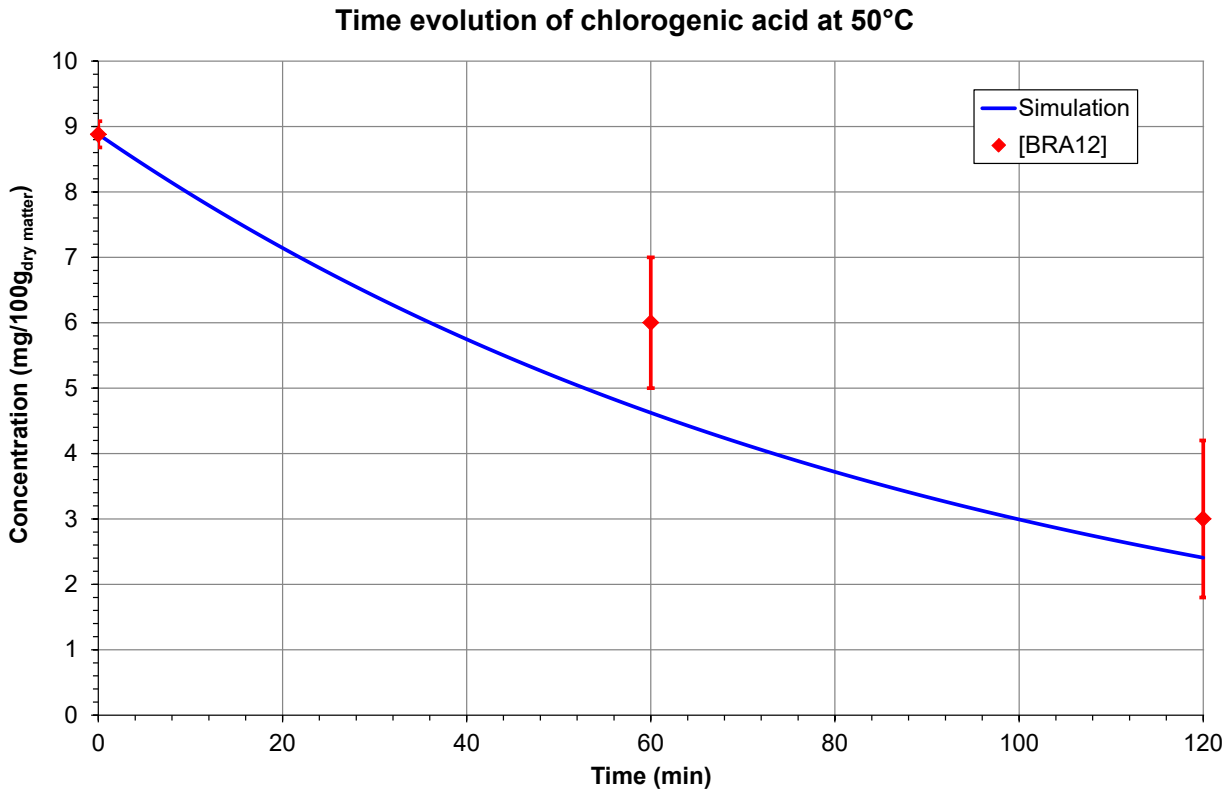
Type	Specified reactor temperature			
Temperature	50°C	70°C	95°C	105°C
Pressure	1 atm			1.3 atm
Step duration	2 h		1 h	

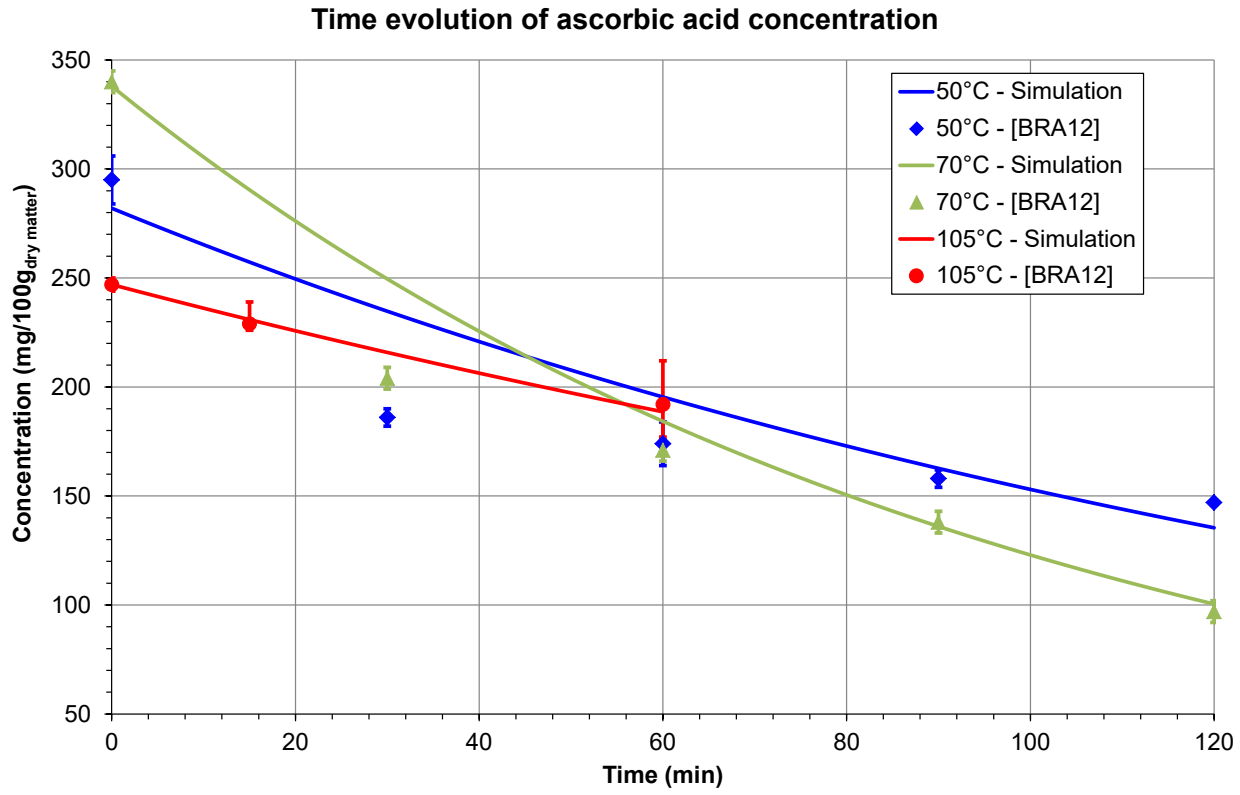
The following screen shot presents the main interface with the scenario on the left and the flowsheet on the right.

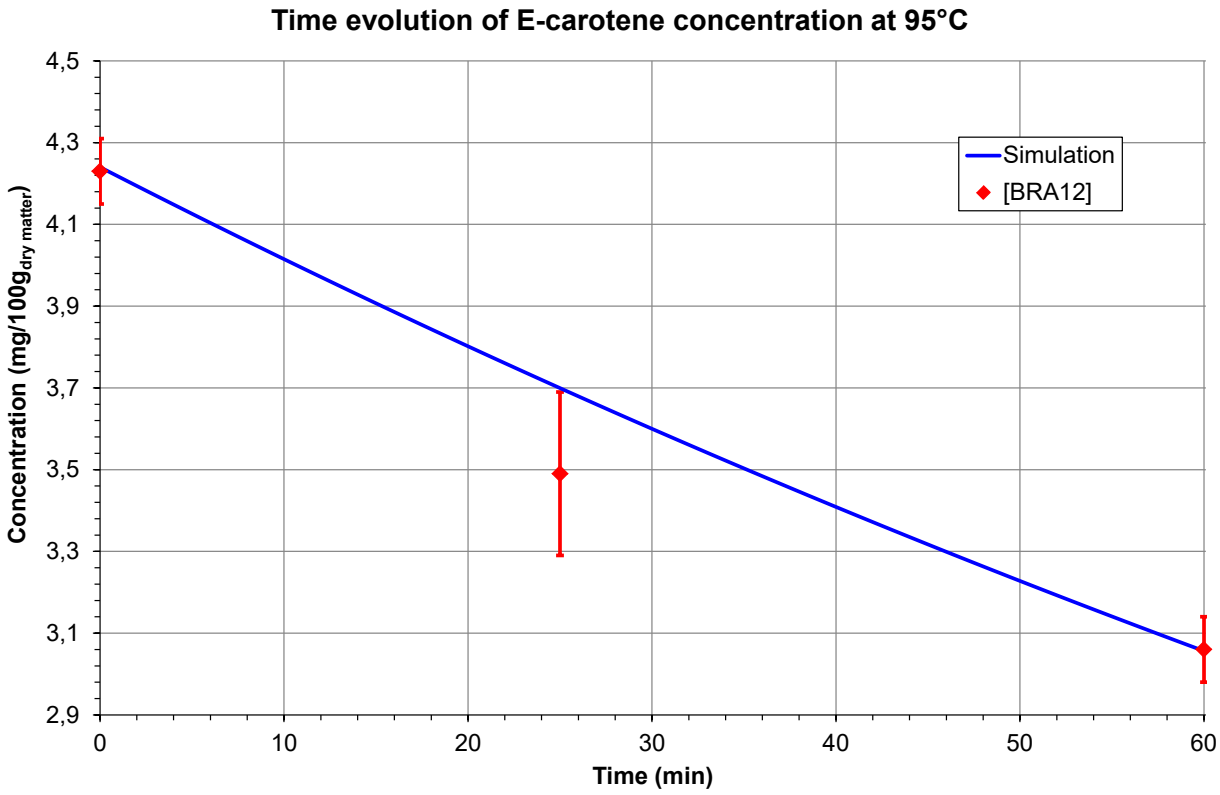


7.2. Results

Comparisons between concentration profiles obtained with BatchReactor software and information given by [BRA12] are provided on the next graphs.







8. REFERENCES

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9. NOMENCLATURE

A_i	Kinetic constant	K
C_i	Molar concentration of the compound I	mol/l
Ea_i	Activation energy	J/mol
k_i^0	Pre-exponential factor	min^{-1}
k_La	Mass transfer coefficient	min^{-1}
R	Perfect gas constant	J/(mol.K)
r_i	Reaction rate	g/(l.s)
T	Temperature	K
$[X]$	Mass concentration of the compound X	g/l
Φ	Mass transfer flow	mol/(l.min)