

## **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  $\beta$ -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.

Access	Free Internet	Restricted to clients	Restricted	Confidential		
		BATCHREA_EX_EN - Tomato sauce Run 050C.pbpr				
CORRESPONDING E		BATCHREA_EX_EN - Tomato sa				
		BATCHREA_EX_EN - Tomato sa	auce Run 095C.pbpi	-		
		BATCHREA_EX_EN - Tomato sa	auce Run 105C.pbpi	r		

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. Fives 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.

#### Energy

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## TABLE OF CONTENTS

1.	INTF	RODUCTION	3
2.	REA		4
3.	CON	IPONENTS	5
4.	THE	RMODYNAMIC MODEL	7
5.	MAS	SS TRANSFER MODEL	8
	5.1.	Model description	8
	5.2.	Configuration of the mass transfer model in BatchReactor	9
6.	REA	CTION MATHEMATICAL MODEL	10
	6.1.	Model description	10
	6.2.	Configuration of the kinetic model using Simulis Reactions	11
7.	SIM	ULATION	18
	7.1.	Process description	18
	7.2.	Results	20
8.	REF	ERENCES	22
9.	NON	IENCLATURE	22

## **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:

 $\checkmark$  Chlorogenic acid oxidation:

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

Namely,

$$C_{16}H_{18}O_9 + O_2 \longrightarrow C_{16}H_{16}O_9 + H_2O_2 \tag{R1}$$

✓ Ascorbic acid oxidation:

Ascorbic acid + 
$$0xygen \rightarrow Dehydroascorbic acid + Hydrogen peroxide$$

Namely,

$$C_6 H_8 O_6 + O_2 \longrightarrow C_6 H_6 O_6 + H_2 O_2$$
 (R2)

✓ Ascorbic acid thermal degradation:

Ascorbic acid  $\rightarrow$  Degraded ascorbic acid

Namely,

$$C_6H_8O_6 \to C_6H_8O_{6\ (degraded)} \tag{R3}$$

✓  $\beta$ -carotene isomerization:

E--- carotene  $\rightarrow$  Z--- carotene

Namely,

$$C_{40}H_{56\,(trans)} \rightarrow C_{40}H_{56\,(cis)}$$

## **3. COMPONENTS**

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

The following components are taken into account in the simulation:

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.

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

The "degraded ascorbic acid" compound is a clone of the ascorbic acid compound. Only the CAS number<sup>1</sup> has been changed (arbitrary number).

<sup>1</sup> 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 <sup>1</sup>	: Arbitrary number
$\checkmark$	Chemical formula	: From literature
$\checkmark$	Molecular weight	: From literature
$\checkmark$	Enthalpy of formation for ideal gas at 25°C	: 0 J/mol
$\checkmark$	Vapor and liquid mass specific heat	: Same as water
$\checkmark$	Vapor pressure	: Parameters chosen to avoid the vaporization
		$Ln(P^0) = -30$ (Equation 101)
$\checkmark$	Vaporization enthalpy	: 0 J/mol
$\checkmark$	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:

Thermodynamic calculator editor				— C	ı x
	This window helps you to define the COMPOUNDS MODEL PA	context of your thermodynamic calculator			
	COMPOUNDS MODEL P/	Bio applications with solids         All the profiles         Bio applications with solids         From activity coefficients         Perfect gas         Not defined         Not defined	00	THERMODYNAMIC MC DOCUMENTATION Thermodynamic assistant Thermodynamic help ADDITIONAL PARAMETERS MODEL INFORMATION WATER-HYDROCARBON PURE WATER	DEL
Export as a PVT file     Sigma profiles  MODIFICATIONS CONFIGURATION Name [New calculator]	Pure liquid fugacity standard state Liquid molar volume Transport properties Enthalpy calculation				
Comments Calculator type Native 💌 Show the expert mode	Comments :				
				Ok	Cancel

#### **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 ( $k_La$ ) in the liquid phase:

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

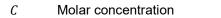
With:

 $\Phi$  Mass transfer flow

mol/(L.h)

mol/L

 $k_L a$  Volumetric mass transfer coefficient in the liquid phase h<sup>-1</sup>



 $C_{G}$   $C_{Gi}$   $C_{Gi}$   $C_{Ui}$   $C_{U}$   $C_{U}$  C

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

Temperature	k∟a
50°C	15.6 h <sup>-1</sup>
70°C	38.4 h <sup>-1</sup>
95°C	105.6 h <sup>-1</sup>
105°C	151.8 h <sup>-1</sup>

## 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:

E-CAROTENE No resistance DRY MATTER No resistance OXYGEN Supplied 15.6 1/h NITROGEN No resistance	E-CAROTENE No resistance Z-CAROTENE No resistance DRY MATTER No resistance OXYGEN Supplied 15.6 1/h NITROGEN No resistance	d • 🛍 🗑				Enter the value for the oxygen k <sub>L</sub> a
Z-CAROTENE No resistance DRY MATTER No resistance OXYGEN Supplied 15.6 1/h NITROGEN No resistance v  por phase properties Vapor phase considered for the mass transfer Head space Dispersed gas	Z-CAROTENE No resistance DRY MATTER No resistance OXYGEN Supplied 15.6 1/h NITROGEN No resistance v  por phase properties Vapor phase considered for the mass transfer Head space Dispersed gas	Compound	Model	Value	^	
DRY MATTER No resistance OXYGEN Supplied 15.6 1/h NITROGEN No resistance  spor phase properties Vapor phase considered for the mass transfer Head space Dispersed gas	DRY MATTER No resistance OXYGEN Supplied 15.6 1/h NITROGEN No resistance  spor phase properties Vapor phase considered for the mass transfer Head space Dispersed gas	E-CAROTENE	No resistance			(depends on the operating temperature
OXYGEN Supplied 15.6 1/h  NITROGEN No resistance  upor phase properties Vapor phase considered for the mass transfer Head space Dispersed gas	OXYGEN Supplied 15.6 1/h  NITROGEN No resistance  upor phase properties Vapor phase considered for the mass transfer Head space Dispersed gas	Z-CAROTENE	No resistance			
NITROGEN No resistance	NITROGEN No resistance	DRY MATTER	No resistance			
v apor phase properties Vapor phase considered for the mass transfer ○ Head space ● Dispersed gas	v apor phase properties Vapor phase considered for the mass transfer ○ Head space ● Dispersed gas	DXYGEN	Supplied	15.6 1/h	100 M	
vapor phase properties Vapor phase considered for the mass transfer Head space Dispersed gas	vapor phase properties Vapor phase considered for the mass transfer Head space Dispersed gas					
Volume % Negligible ~	Volume % Negligible ~	por phase propert Vapor phase cons	ies		~	
		por phase propert Vapor phase cons O Head space	ies sidered for the mass transfe		~	

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:

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

✓ Rate of the ascorbic acid oxidation:

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

✓ Rate of the ascorbic acid degradation:

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

✓ Rate of  $\beta$ -carotene isomerization:

$$r_{Caro} = k_{Caro}^{0} \times \exp\left(\frac{-Ea_{Caro}}{RT}\right) \times [E-Carotene]$$
(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	$k_{ACHL}^0 = 5180 \ min^{-1}$
		$Ea_{ACHL} = 35100 J. mol^{-1}$
	25°C – 95°C	$k_{AASC}^0 = 12300 \ min^{-1} \cdot 100 g/mg$
	20 0 00 0	$Ea_{AASC} = 37400 J. mol^{-1}$
Ascorbic acid (AASC)	25°C – 125°C	$k_{AASC\ (degrad.)}^{0} = 1,75e6\ min^{-1}$
		$A_{AASC \ (degrad.)} = 7480 \ K$
β-Carotene (Caro)	95°C – 125°C	$k_{Caro}^{0} = 2070 \ min^{-1}$
		$Ea_{Caro} = 39300 J. mol^{-1}$

## 6.2. Configuration of the kinetic model using Simulis Reactions

The four reactions were described in Simulis Reactions:

Chemical reactions editor						—		×
CHEMICAL REACTIONS	This win	ndow helps you to	manage you	r chemical reac	tion list			
REACTIONS	#	Name		Туре	Physical state	Model		
🕂 Add a reaction	1	Chlorogenic Ac			Liquid	User "in	terpreted	-
🕅 Edit this reaction	2	Ascorbic Acid +	+ O2 -> Dehy l	Kinetic	Liquid		terpreted	
Clone this reaction	3 🕻	Ascorbic Acid -			Liquid		terpreted	I
Cione this reaction	4 🛯	Z E-Carotene -> 3	Z-Carotene (I I	Kinetic	Liquid	User "in	terpreted	r
X Delete this reaction								
🗊 Literal expressions								
ORDER								
Move up the reaction								
Move down the reaction								
MODIFICATIONS								
🔊 Undo								
🔊 Redo								
PACKAGE								
🛒 Show the package manager								
🎢 Import a package	Comme	nts:						
🥤 Build a package								
					[	Ok	Cano	tel

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

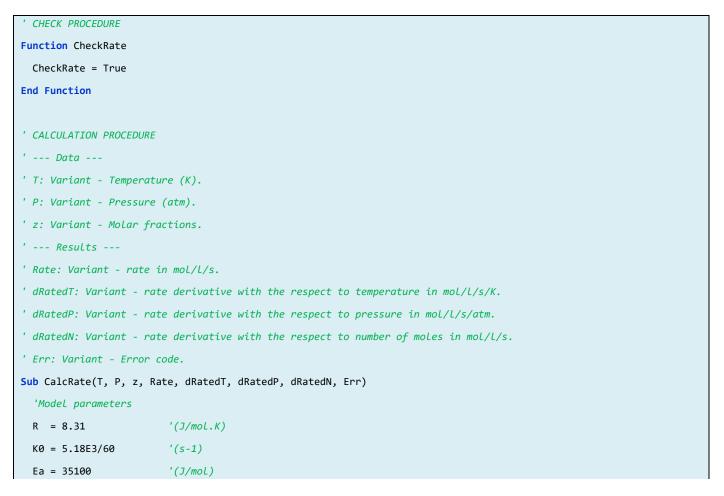
http://en.wikipedia.org/wiki/VBScript

All reactions take place in the liquid phase.

The heat of reaction of each reaction is assumed to be 0.

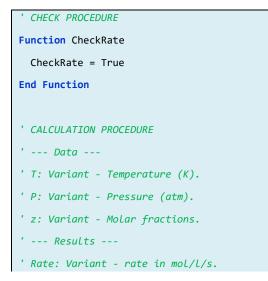
CHEMICAL REACTION         This window helps you to define the context of your chemical reaction         ID: [590393CC-8209-4AB7-ACB8-9E3F064AF003]         ID: [5907064         ID: [59070707         ID: [5907070707         Properties         Stoichiometry and orders         Name       CAS Registry Number® or         VATER       T722-18-5       0 </th <th>Chemical reaction editor</th> <th></th> <th></th> <th></th> <th>_</th> <th>- 0 x</th>	Chemical reaction editor				_	- 0 x
<ul> <li>Equilibrium</li> <li>Kinetic</li> <li>Instantaneous</li> <li>TOOLS</li> <li>PDF Export (Print)</li> <li>MODIFICATIONS</li> <li>Concentration model</li> <li>Molar concentration</li> <li>Reado</li> <li>HELP</li> <li>Technical help</li> <li>Properties</li> <li>Name</li> <li>CAS Registry Number® or</li> <li>Stoichiometry and orders</li> <li>Name</li> <li>CAS Registry Number® or</li> <li>Stoichiometry Direct</li> <li>Reverse</li> <li>WATER</li> <li>T732-18-5</li> <li>O</li> <li>O</li> <li>O</li> <li>Concentration</li> <li>Concentration</li> <li>Concentration</li> <li>Concentration</li> <li>Concentration</li> <li>Concentration</li> <li>Concentration</li> <li>Rate model</li> <li>User 'Interpreted'</li> <li>Properties</li> <li>Stoichiometry and orders</li> <li>Name</li> <li>CAS Registry Number® or</li> <li>Stoichiometry Direct</li> <li>Reverse</li> <li>NASCORBIC ACID</li> <li>Stoichionetry</li> <li>Direct</li> <li>Reverse</li> <li>CHUROGENIC ACID</li> <li>Stoichionetry</li> <li>O</li> <li>O</li>     &lt;</ul>				nical reaction		
Vindo         Rate model         User 'interpreted''           Image: Properties         Stoichiometry and orders           Name         CAS Registry Number® or         Stoichiometry         Direct         Reverse           WATER         7732-18-5         0         0         0           HVDROGEN PEROXIDE         7722-84-1         1         0         0           ASCORBIC ACID         50-81-7         0         0         0           DEGRADED ASCORBIC ACID         12345-67-4         0         0         0           QUINONE         22010-02-1         -1         1         0         0           DEHYDROASCORBIC ACID         55410-00-9         0         0         0         0           Properties         55310-01-5         0         0         0         0         0	<ul> <li>Kinetic</li> <li>Instantaneous</li> <li>TOOLS A</li> <li>PDF Export (Print)</li> </ul>	Name Cl User ID Physical state Li Reaction heat Su	nlorogenic Acid + O2 -> Quinon quid μpplied by the user	e + H2O2 (Fresh to	imatoes -> Concen	tate Activated
Properties         Stoichiometry and orders           Name         CAS Registry Number® or         Stoichiometry and orders           WATER         7732-18-5         0         0           HYDROGEN PEROXIDE         7722-84-1         1         0         0           AscORBIC ACID         50-81-7         0         0         0           DEGRADED ASCORBIC ACID         12345-67-4         0         0         0           QUINONE         22010-04-4         1         0         0           DEHYDROASCORBIC ACID         5510-02-1         -1         1         0           DEHYDROASCORBIC ACID         5510-01-5         0         0         0           DEHYDROASCORBIC ACID         5510-02-1         -1         0         0           DEHYDROASCORBIC ACID         5510-01-5         0         0         0           T-CAROTENE         55210-02-1         0         0         0           JPY MATTER         55000-36-7         0         0         0	🔊 Undo	contentiation model		<u> </u>		
Ok Cancel		Name WATER HYDROGEN PEROXIDE ASCORBIC ACID DEGRADED ASCORBIC ACID CHLOROGENIC ACID QUINONE DEHYDROASCORBIC ACID E-CAROTENE Z-CAROTENE DRY MATTER	7732-18-5 7722-84-1 50-81-7 12345-67-4 55010-02-1 22010-04-4 555410-00-9 55310-01-5 55210-02-1	Stoichiometry 0 1 0 0 -1 1 0 0 0 0 0 0	Direct 0 0 0 1 0 0 0 0 0 0 1 1 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

The VBS code for the (R1) reaction is the following:



```
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")
                = Quantity.Convert(Vml,"cm3/mol","1/mol")
  Vm1
  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:



```
' 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")
  Vm1
                = Quantity.Convert(Vml,"cm3/mol","1/mol")
                = Repository.QuantityByName("Molar mass")
  Set MwQty
  'Calculation of the concentrations
  CASN_0xygen = "7782-44-7"
  For i=1 To ThermoCalculator.Compounds.Count
    With ThermoCalculator.Compounds.Items(i-1)
     If (.CasRegistryNumber = CASN_Oxygen) Then
          ipos_0xygen = 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</pre>
```

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



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CASN_AscorbicAcid = "50-81-	7"				
For i=1 To ThermoCalculator	For i=1 To ThermoCalculator.Compounds.Count				
With ThermoCalculator.Com	npounds.Items(i-1)				
<pre>If (.CasRegistryNumber</pre>	= CASN_AscorbicAcid) Then				
ipos_AscorbicAcid =	= i-1				
Mw_AscorbicAcid =	<pre>MwQty.Convert(.Mw.Value,.Mw.UnitName,"g/mol")</pre>				
C_AscorbicAcid =	<pre>z(ipos_AscorbicAcid)*Mw_AscorbicAcid/Vml</pre>				
End If					
End With					
Next					
'Calculation of the reaction	on rate				
If (T >= 298.1 And T <= 398	3.2) Then 'Temperature between 25°C and 125°C				
Rate = K*C_AscorbicAcid	'(g/L.s)				
Rate = Rate/Mw_Ascorbic	Acid '(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)
```

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K = K0*exp(-Ea/(R*T)) '(s-1)	
'Calculation of the molar volume	
Vml=ThermoCalculator.PCalcVml(T,P,z)	)
'Units conversion	
Set Quantity = Repository.Quantity	/ByName("Molar volume")
Vml = Quantity.Convert(V	/ml,"cm3/mol","l/mol")
Set MwQty = Repository.Quantity	/ByName("Molar mass")
'Calculation of the concentrations	
CASN_ECarotene = "55310-01-5"	
For i=1 To ThermoCalculator.Compound	ds.Count
With ThermoCalculator.Compounds.It	cems(i-1)
<pre>If (.CasRegistryNumber = CASN_EC</pre>	Carotene) Then
<pre>ipos_ECarotene = i-1</pre>	
Mw_ECarotene = MwQty.Conve	ert(.Mw.Value,.Mw.UnitName,"g/mol")
C_ECarotene = z(ipos_ECar	rotene)*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				
Туре	Closed vapor-liquid			
Global volume (vapor + liquid)	500 I			
Head space type	Air			

The initial conditions are presented in the following table. For the case where  $T = 105^{\circ}C$ , 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			1.3 atm
	Experimental concentration [BRA12] (mg/100g <sub>dry matter</sub> )				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			

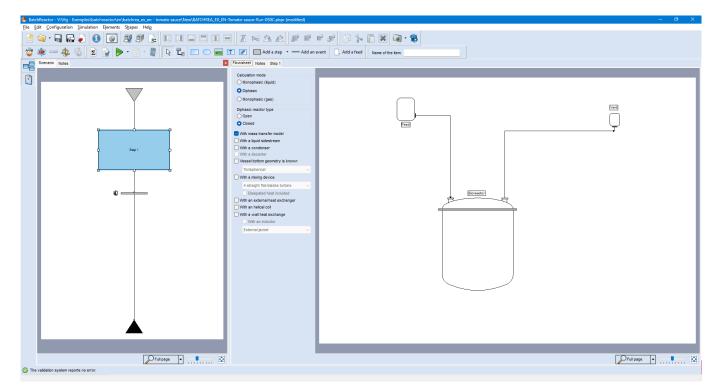
An air stream continuously feeds the reactor in order to make sure that oxygen is kept in excess in the gas phase The characteristics of this stream are:

Temperature	50°C 70°C 95°C 105			105°C	
Pressure		1.3 atm			
Total flow rate	10 kg/h				
Mole fractions					
Oxygen		0.2	21		
Nitrogen		0.	79		

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

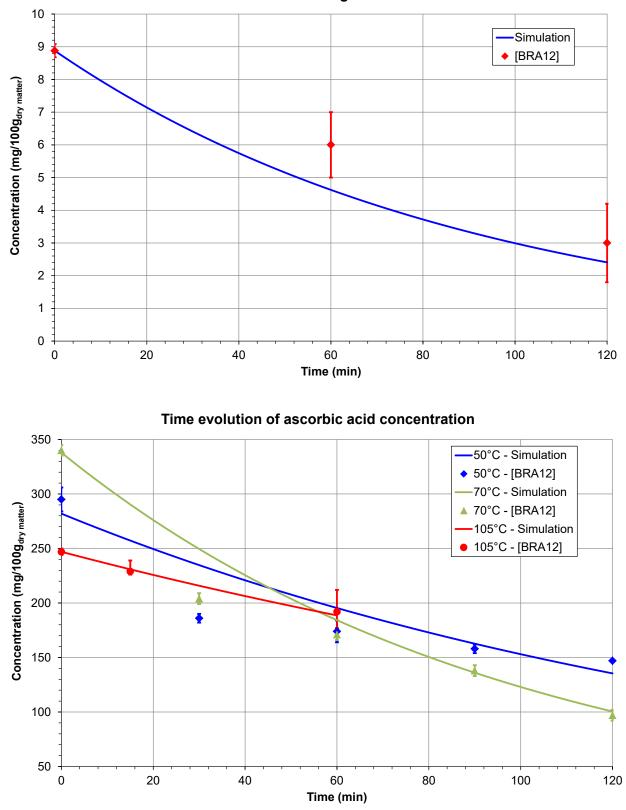
Туре	Specified reactor temperature			
Temperature	50°C	70°C	95°C	105°C
Pressure		1 atm		1.3 atm
Step duration	2 h		1 h	

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

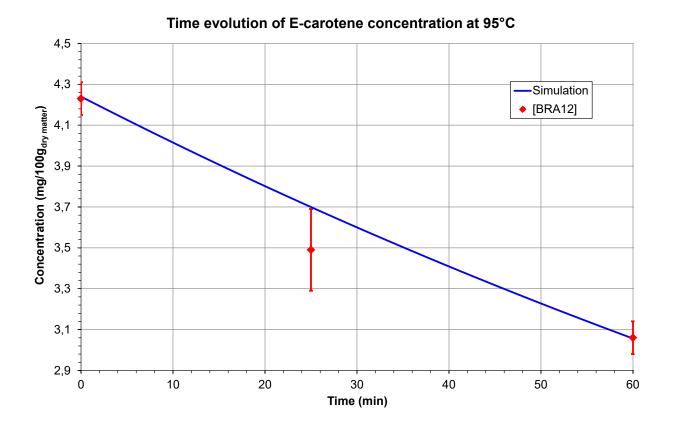


## 7.2. <u>Results</u>

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



#### Time evolution of chlorogenic acid at 50°C



- [BRA12] BRANDAM C., MEYER X., ROLAND M., "Application et validation industrielle d'un modèle prédictif de la qualité nutritionnelle de produits à base de tomate au cours des procédés de fabrication", DGAL Convention a13 PACA 05 12-1
- [ROW21] 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 (2021)

## 9. NOMENCLATURE

$A_i$	Kinetic constant	К
C <sub>i</sub>	Molar concentration of the compound I	mol/l
Ea <sub>i</sub>	Activation energy	J/mol
$k_i^0$	Pre-exponential factor	min <sup>-1</sup>
$k_L a$	Mass transfer coefficient	min <sup>-1</sup>
R	Perfect gas constant	J/(mol.K)
r <sub>i</sub>	Reaction rate	g/(l.s)
Т	Temperature	К
[X]	Mass concentration of the compound X	g/l
Φ	Mass transfer flow	mol/(I.min)