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BATCHREACTOR APPLICATION EXAMPLE

SCALE-UP OF A CHLORINATION REACTOR

EXAMPLE PURPOSE
The main interest of this example is the scale-up of a chlorination reactor. The chlorination of o-chlorotoluene is performed in a vapor-liquid reactor. The heating/cooling device of the reactor and the condenser geometry are specified. During the reaction step, the temperature level in the reactor is controlled with a PID.

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CORRESPONDING BATCHREACTOR FILE	*BATCHREA_EX_EN - Chlorination reactor.pbpr*

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Energy

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1. INTRODUCTION

This example deals with the chlorination of o-chlorotoluene in a mechanically agitated gas-liquid reactor. The following technological elements are taken into account:

- ✓ The heating/cooling device of the tank,
- ✓ The mixing system,
- ✓ The condenser.

The recipe consists of two steps. The first step is the heating of the initial load to the temperature necessary to start the reaction. The second step is the reaction step. The reaction starts with the injection of one of the reactants. During this step, the temperature level in the reactor is controlled by a PID.

Finally, a scale-up of this reactor to increase the volume by a factor 3 is detailed.

2. REACTION MECHANISM

The first chlorination reaction adds a chlorine group to the o-chlorotoluene in order to form the benzyl dichloride:

$$o\text{–}\,Chlorotoluene + Chlorine \longrightarrow Benzyl\ dichloride + Hydrogen\ chloride$$

Namely,

$$C_7H_7Cl + Cl_2 \longrightarrow C_7H_6Cl_2 + HCl \qquad \text{(R1)}$$

The second chlorination adds a chlorine group to the benzyl dichloride in order to form the benzotrichloride:

$$Benzyl\ dichloride + Chlorine \longrightarrow Benzotrichloride + Hydrogen\ chloride$$

Namely,

$$C_7H_6Cl_2 + Cl_2 \longrightarrow C_7H_5Cl_3 + HCl \qquad \text{(R2)}$$

This reaction is an undesired side reaction, the product of interest being the benzyl dichloride.

3. COMPONENTS

Components which are considered in the simulation are:

Name	Formula	CAS number[1]
o-Chlorotoluene	C_7H_7Cl	95-49-8
Benzyl dichloride	$C_7H_6Cl_2$	98-97-3
Benzotrichloride	$C_7H_5Cl_3$	98-07-7
Chlorine	Cl_2	7782-50-5
Hydrogen chloride	HCl	7647-01-0
Nitrogen	N_2	7727-37-9

The compounds are taken from the Simulis Thermodynamics standard database, thermodynamics calculation engine used in BatchReactor. The thermophysical parameters stored in this database are the DIPPR recommended values [ROW23].

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

4. THERMODYNAMIC MODEL

The NRTL [REN68] thermodynamic model is used to model the vapor-liquid equilibria. Binary interaction parameters are defined for the following three binaries of the systems:

Binary	C_{ij}	C_{ji}	α_{ij}	C_{ij}^T	C_{ji}^T	α_{ij}^T
o-chlorotoluene – Benzyl dichloride	-707.3	775.31	0.1939	0	0	0
o-chlorotoluene – Benzotrichloride	-1246	1463.5	0.1584	0	0	0
Benzyl dichloride – Benzotrichloride	64.339	-79.04	0.4097	0	0	0

5. REACTION MATHEMATICAL MODEL

The kinetics of the transformation of o-chlorotoluene in benzyl dichloride and then in benzotrichloride by reaction with chlorine are modeled by an Arrhenius law:

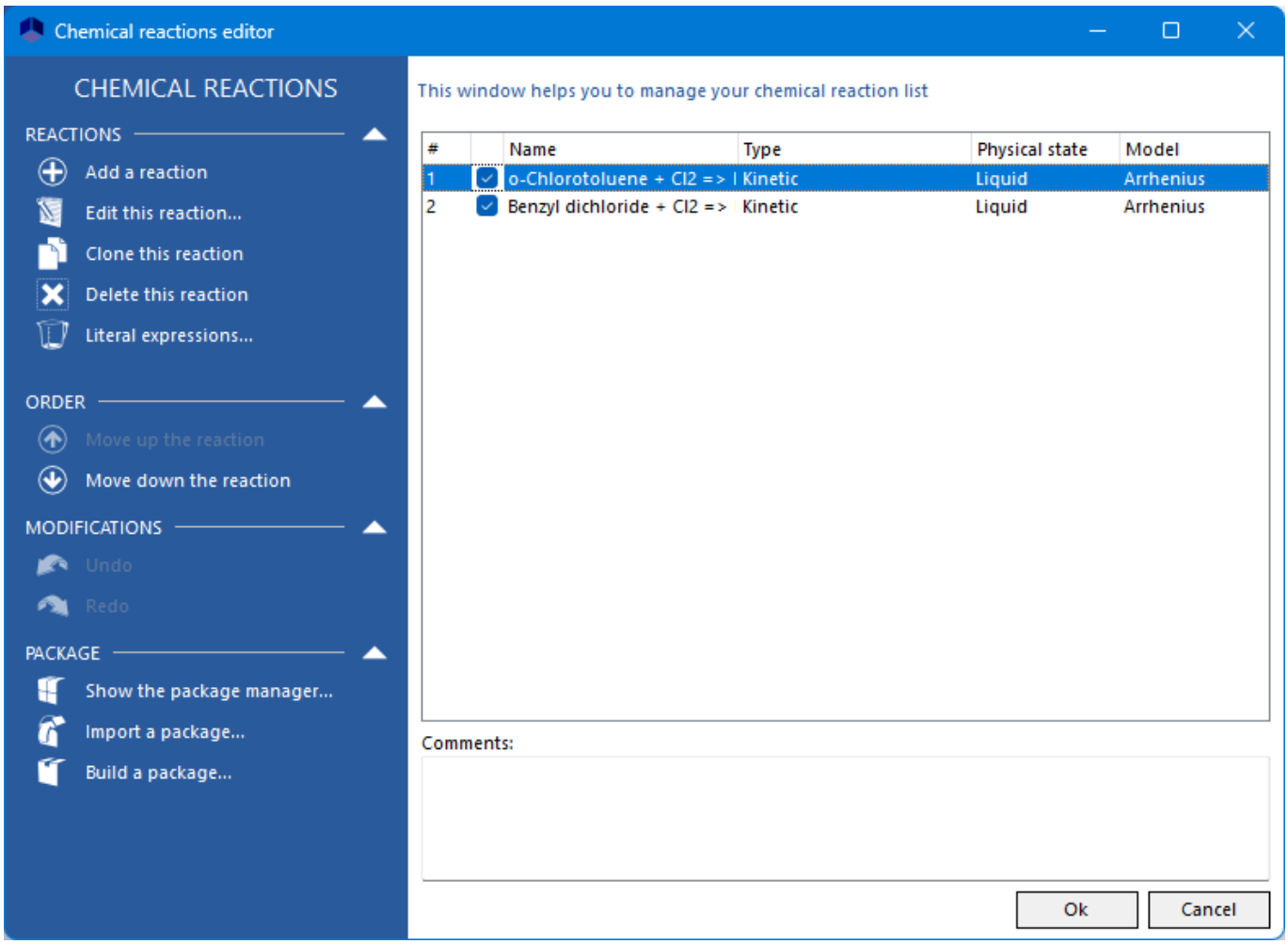
$$r_i = k_i \times exp\left(\frac{-Ea_i}{RT}\right) \times C_{Ai} \times C_{Bi}$$

The kinetics parameters for each reaction are presented in the following table:

Reaction	C_{Ai} (mol/l)	C_{Bi} (mol/l)	k_i (l/mol/s)	Ea_i (J/mol)
R1	o-chlorotoluene	Chlorine	$2.7203e^{17}$	130 320
R2	Benzyl dichloride	Chlorine	580	42 200

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 following screenshot.



These two reactions follow a “classic” Arrhenius law. Thus, they are described with the standard Simulis Reactions interface.

All reactions take place in the liquid phase.

The heat of reaction of each reaction is computed from standard enthalpies of formation.

7. SIMULATION

7.1. Process description

7.1.1. Reactor

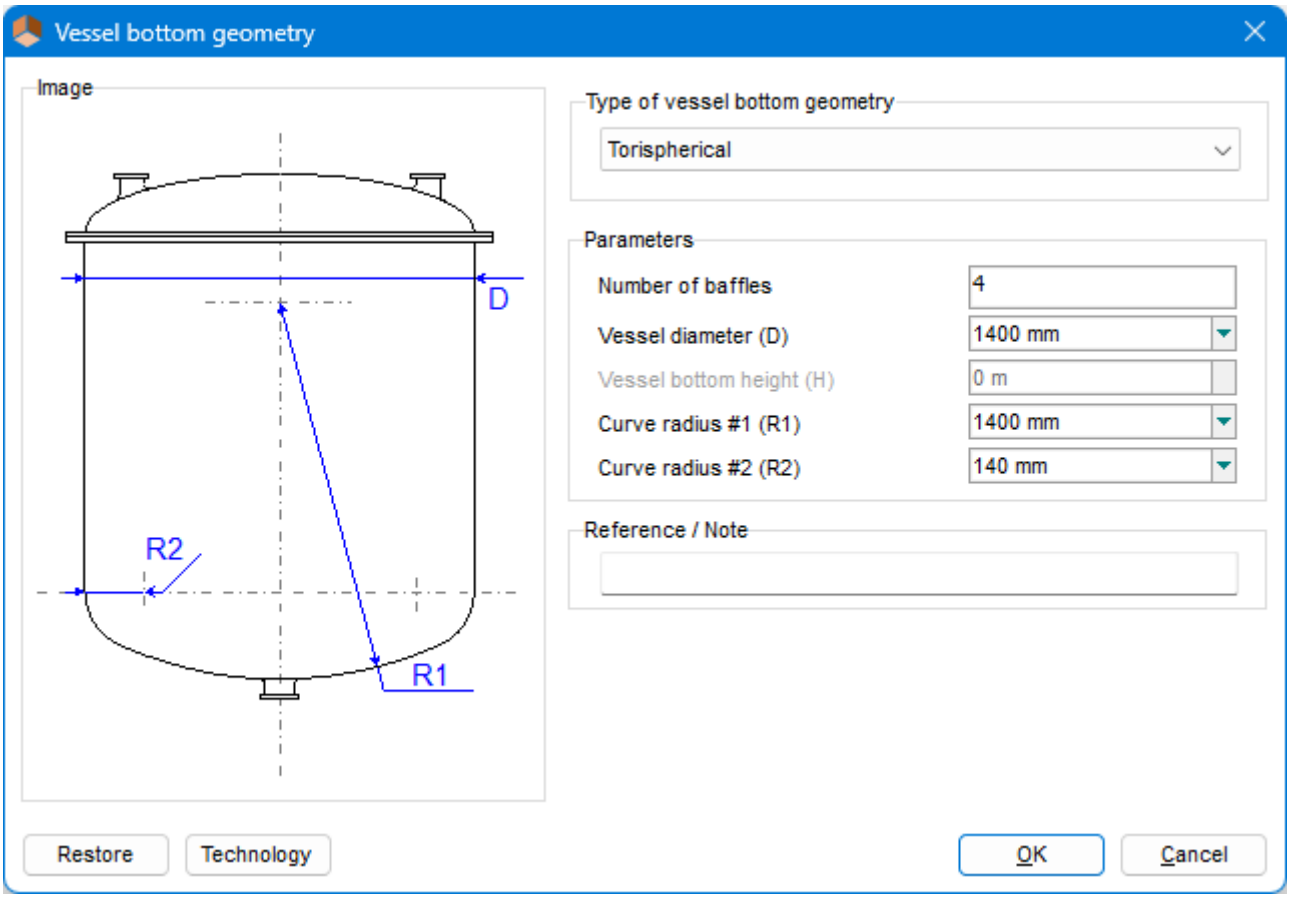
The reactor used for the chlorination of o-chlorotoluene is a closed two-phase vapor-liquid reactor:

Reactor characteristics	
Volume	3 m^3
Head space	Nitrogen

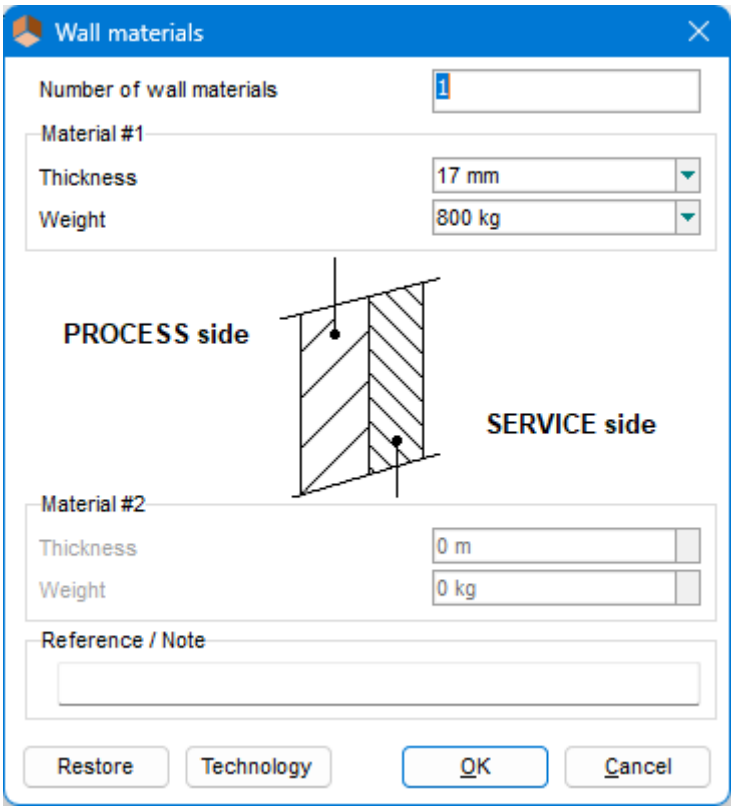
The initial conditions are presented in the following table:

Initial conditions	
Temperature	25°C
Pressure	1 atm
Initial load	
o-Chlorotoluene	2 400 kg

The vessel bottom geometry is described in the screen capture below:



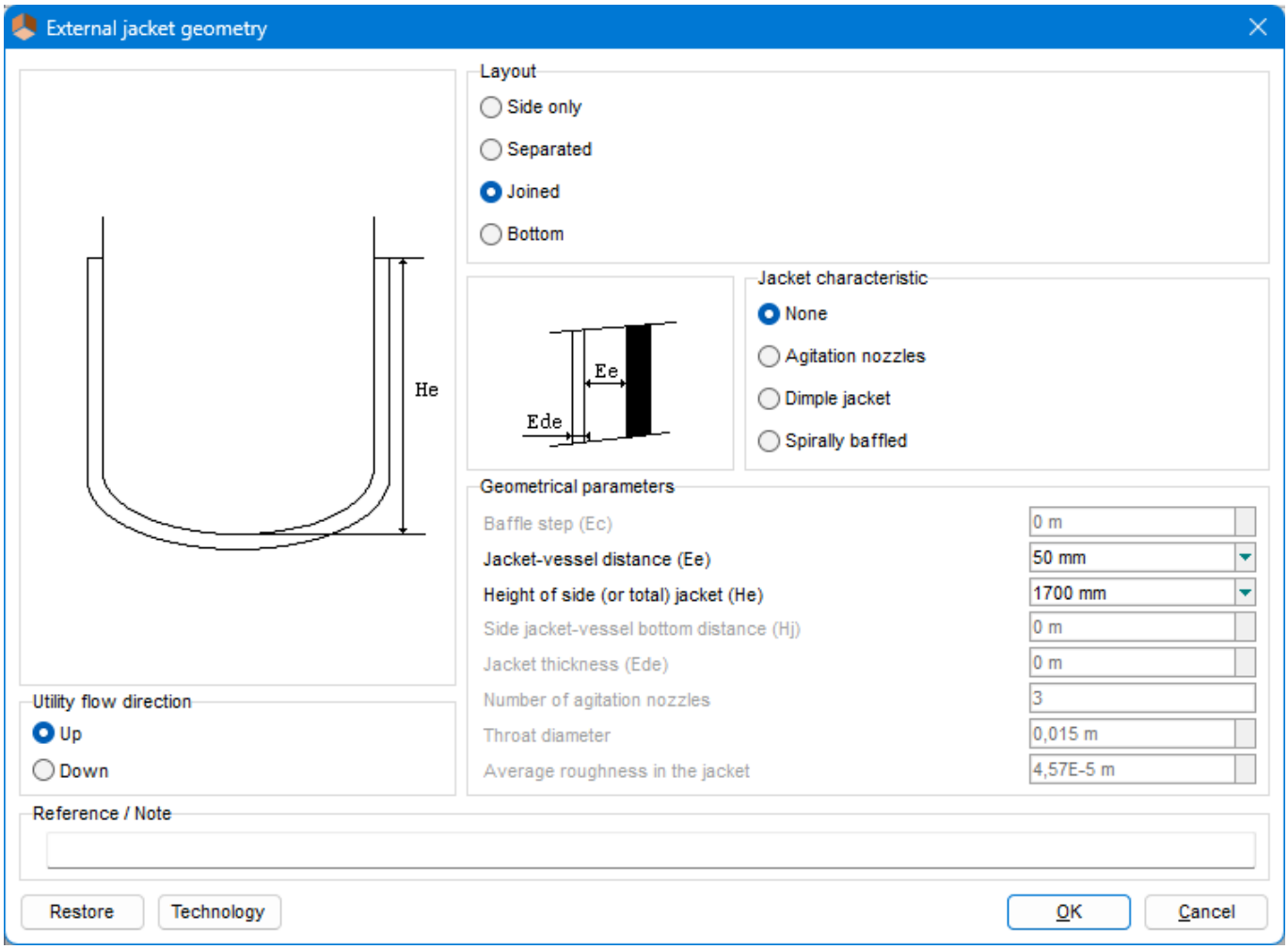
The reactor is made of stainless steel. The weight of the tank is specified because the thermal inertia in the wall will be taken into account in the simulation.



The thermal conductivity of the stainless steel is taken equal to 15.3 W/m/K and its mass specific heat to 500 J/kg/K. These properties are specified for each operating step.

7.1.2. Heating/cooling device

The wall heat exchanger used in this simulation is detailed in the following screenshot:

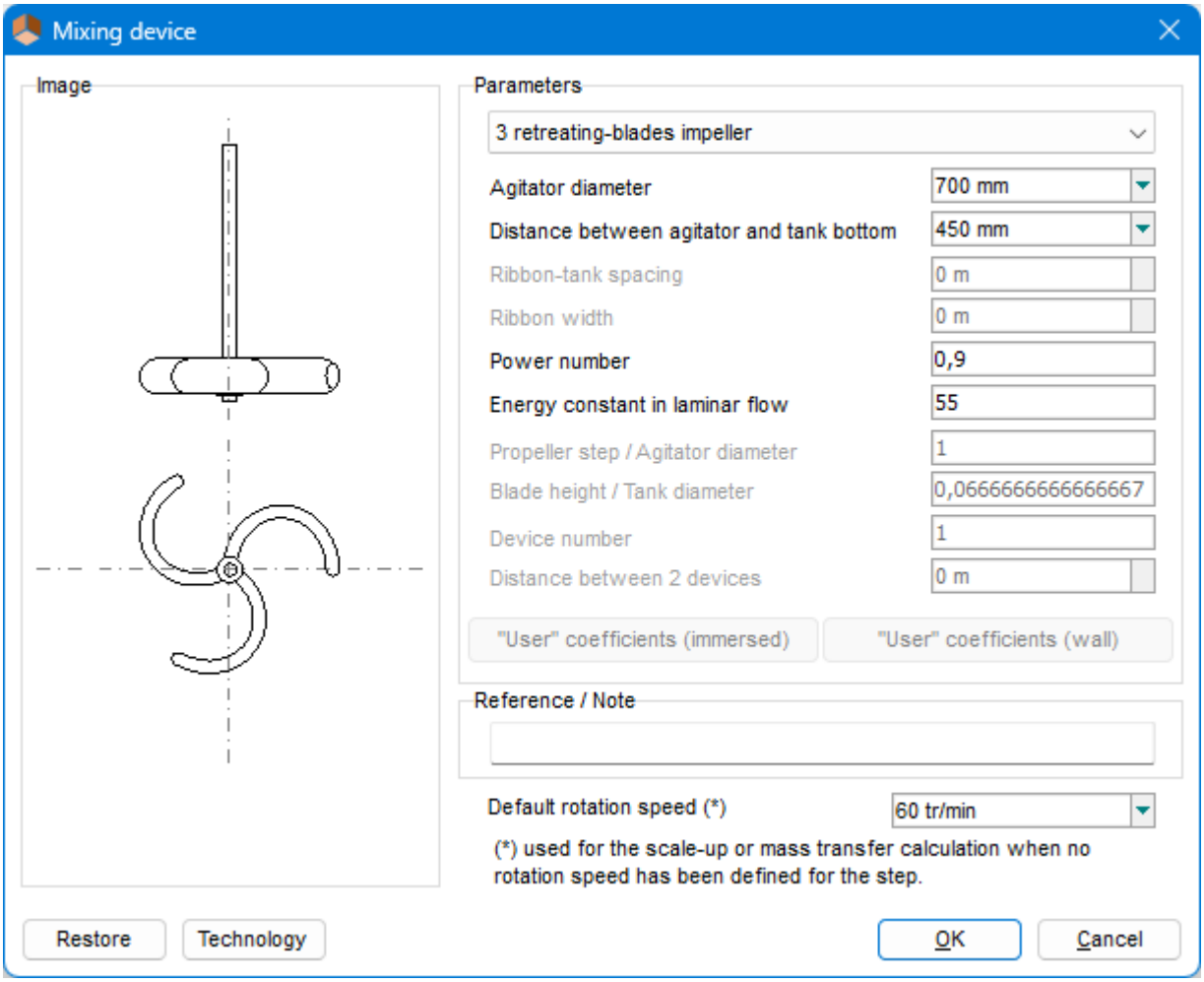


The thermal fluids used are detailed in the table below:

First step: heating fluid	
Type	Saturated steam
Pressure	6 bar abs.
Mass flow rate	200 kg/h
Second step: cooling fluid	
Type	Water
Inlet temperature	25°C
Nominal mass flow rate	4 000 kg/h

7.1.3. Mixing device

The characteristics of the mixing device are shown in the next figure. The rotational speed is 90 rpm for each operating step.



	The **Power number** and **Energy constant in laminar flow** are used when scale-up calculations are performed. The values displayed by default are usual guess for standard geometries of each impeller type and for a classical implementation in the tank. Before all calculations, the adequacy of these values with the actual size and implementation of the mixing system should be verified.

	The rotation speed (*i.e.* the rotational speed of the agitator) is used for extrapolation or mass transfer calculations only for steps in which this value is not specified.

7.1.4. Condenser

In this example, a two stages condenser is used. The parameters of the two stages are shown in the following table. The parameters are the same for the two steps.

	1st stage	2nd stage
Calculation type	U and A given	
Heat exchange coefficient ($kcal.h^{-1}.m^{-2}.°C^{-1}$)	300	
Heat exchange area (m^2)	15	0.5
Service fluid		
Type	Water	Other
Inlet temperature (°C)	20	-15
Flow rate (kg/h)	3 000	100
Number of reference point	-	1
Reference temperature (°C)	-	-15
Heat capacity ($cal.g^{-1}.K^{-1}$)	-	0.7933

7.1.5. PID controller

The parameters of the PID used to control the temperature of the reactor during the reaction steps are:

Temperature specification	
Minimum temperature	59°C
Set point temperature	62°C
Maximum temperature	65°C
Command variable	
Type	Service fluid flow rate
Minimum flow rate	1 kg/h
Maximum flow rate	10 000 kg/h
Controller	
Control type	Feedback
Gain	-5
Ti	500 s
Td	0 s
Sample rate	10 s
Valve	
Equation type	Exponential
Cv	30

7.1.6. Feeds

A continuous nitrogen flux is fed during the whole operation (*i.e.* during the two steps):

Temperature	25°C
Pressure	1 atm
Nitrogen flow rate	1 kg/h

A continuous chlorine flux (reactant) is fed during the second operating step (reaction step):

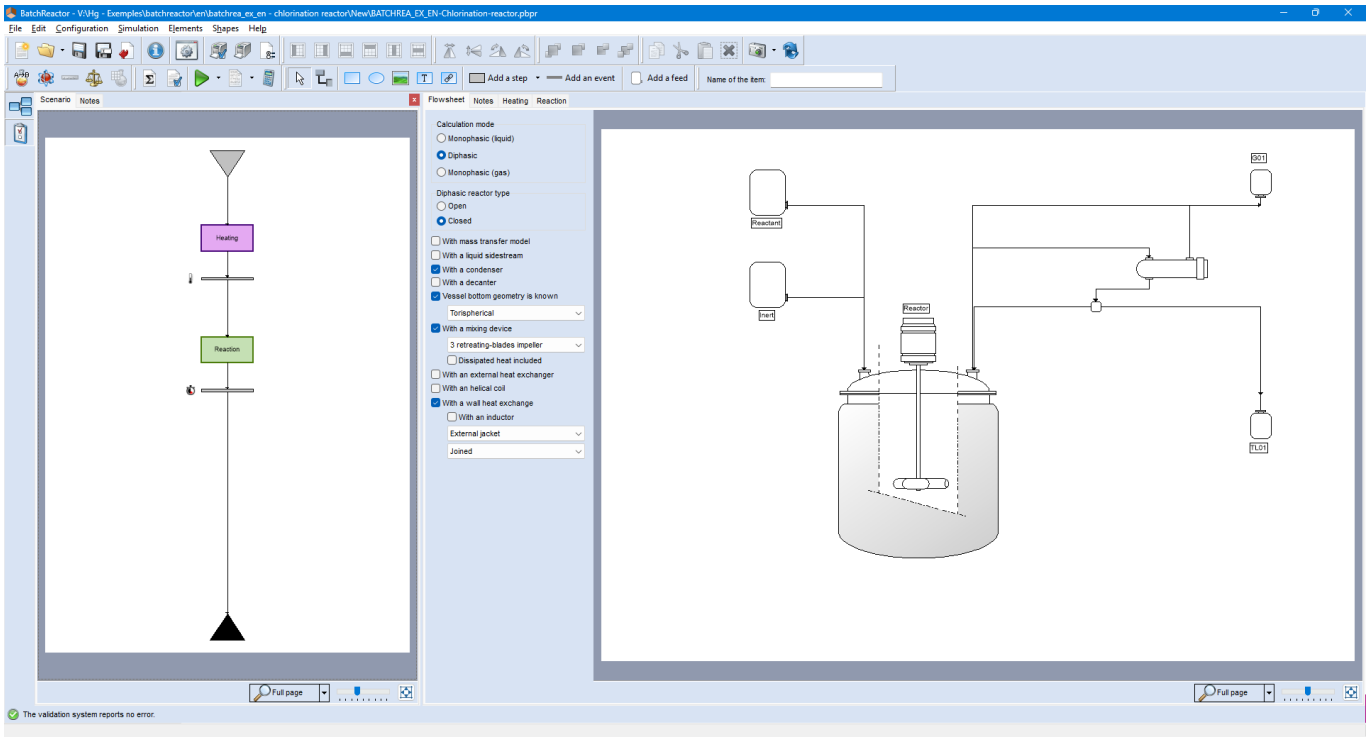
Temperature	25°C
Pressure	3 bar abs.
Chlorine flow rate	60 kg/h

7.1.7. Recipe

The recipe consists in two operating steps. In the first one, the initial load is heated to 58°C under total reflux. No reaction takes place during this step. After this step, the reactant (chlorine) is fed during 13 hours. During this reaction step, the temperature in the reactor is controlled at 62°C by a PID (action on the service fluid flow rate). The parameters are summarized in the following table:

Parameter	First step: Heating	Second step: Reaction
Type	Variable heat duty	Specified reactor temperature with a thermal device
Reactor pressure	1 atm	
Reflux ratio	1	
Nitrogen feed	Open	
Chlorine feed	Closed	Open
Stop event	58°C in the reactor	13 h of reaction

The scenario is presented on the left of the following screen shot and the flowsheet on the right part.



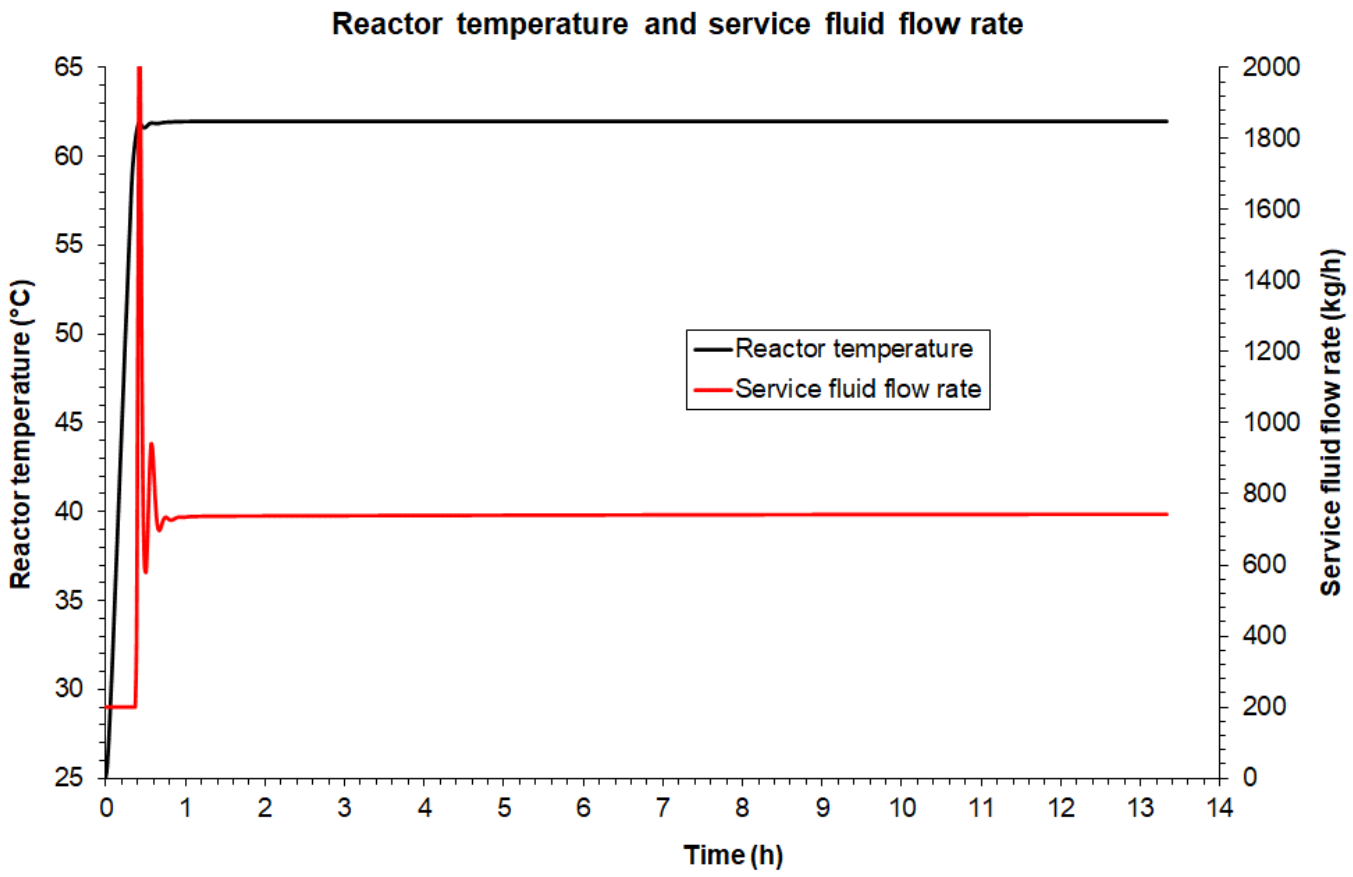
7.2. “Tips & Tricks”

To have smoother profiles during the first part of the reaction step, the time between each output can be decreased to 60 s (instead of the default value of 600 s) in the report parameters tab.

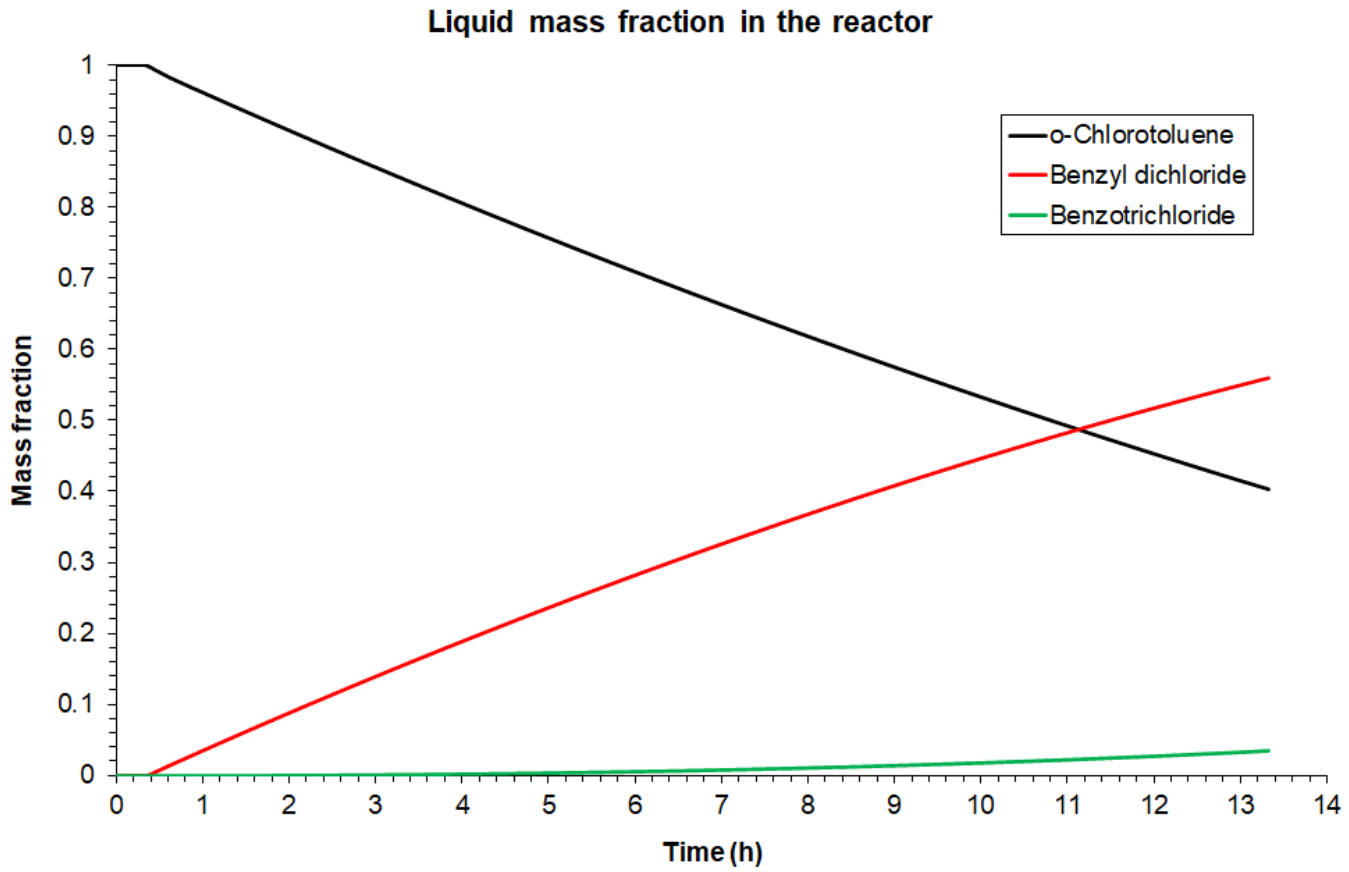
In a first step, to analyze the effect of the PID, the time of the reaction step can be reduced to 2 h instead of 13 h.

7.3. Results

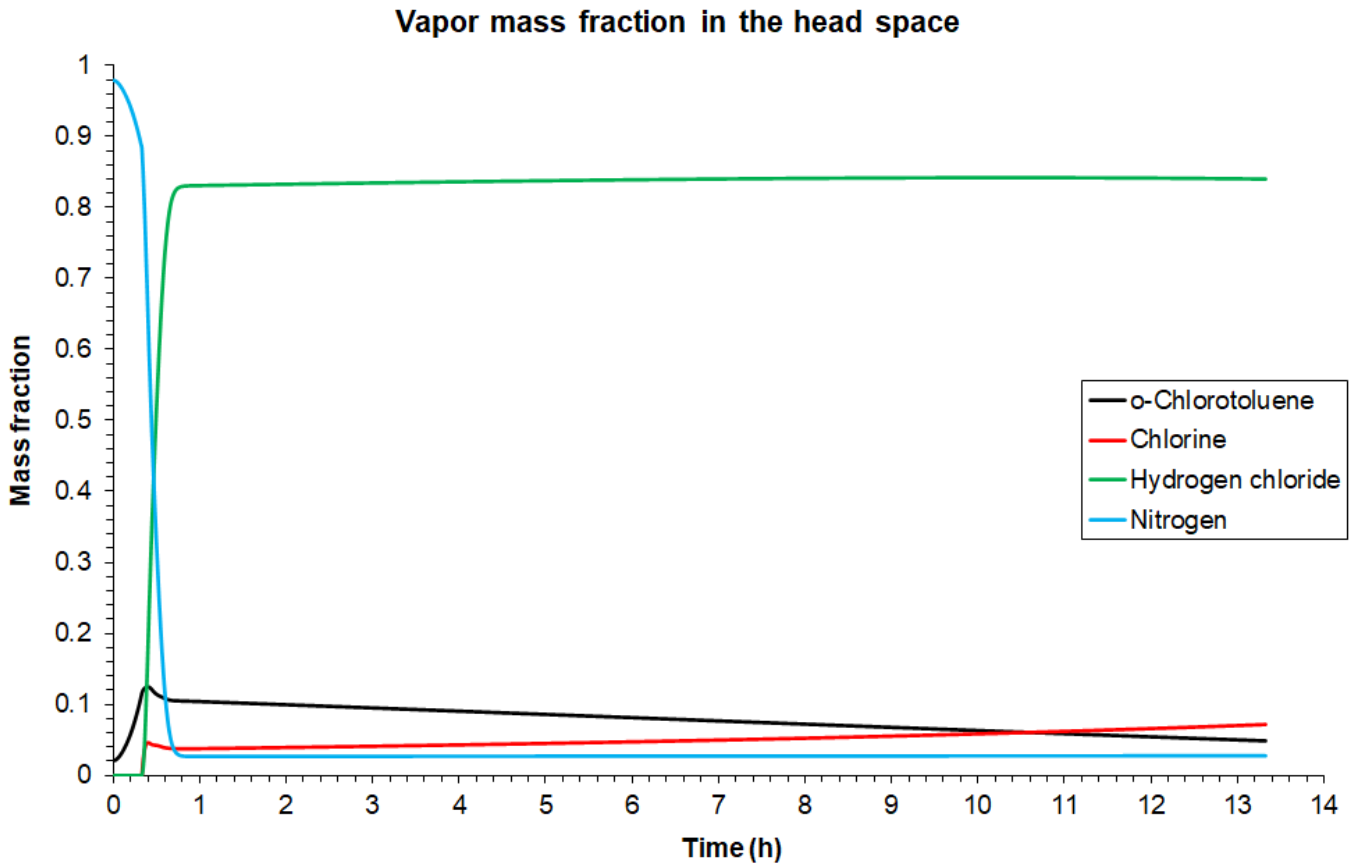
The following figure shows the evolution of the reactor temperature and the service fluid flow rate. During the heating step, the reactor temperature increases almost linearly from the initial temperature (25°C) to the desired temperature (58°C). During this step, the service fluid flow rate (steam) is constant. This step lasts 19,5 min. During the reaction step, the controller accurately controls the reactor temperature to 62°C. The service fluid flow rate (user defined fluid) shows strong variation in the beginning of this step due to the action of the controller to control the reactor temperature.



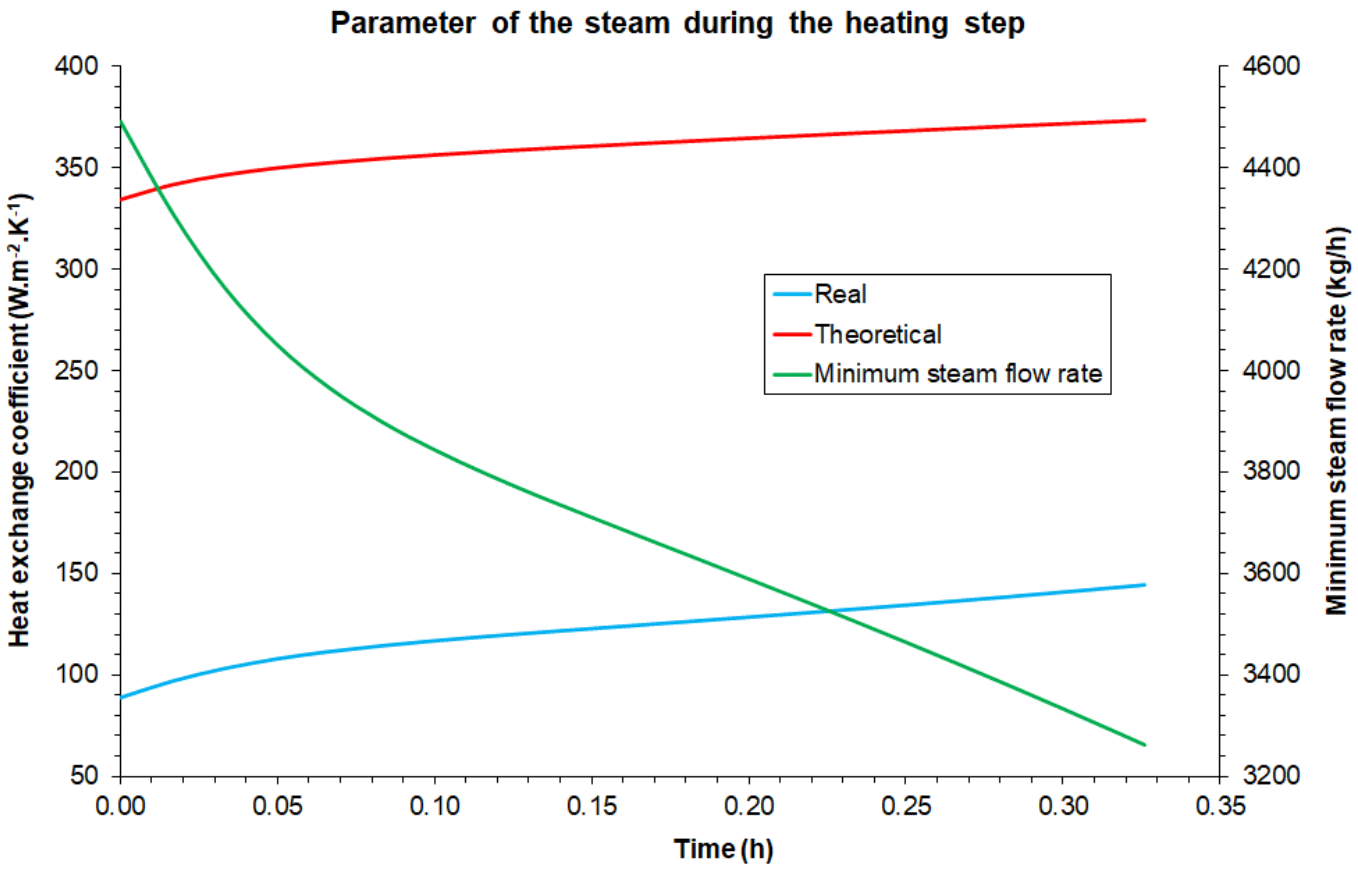
After the first 20 minutes of heating, the o-chlorotoluene content decreases due to the chlorination. Even if the benzyl dichloride reacts to form the benzotrichloride, during the 13 h of the reaction, the amount of the benzyl dichloride is greater than the one of the benzotrichloride.



During the heating step, the nitrogen is progressively replaced by o-chlorotoluene. During the reaction step, the head space of the reactor is mainly composed of hydrogen chloride; chlorine, o-chlorotoluene and nitrogen are also present but in smaller quantities.

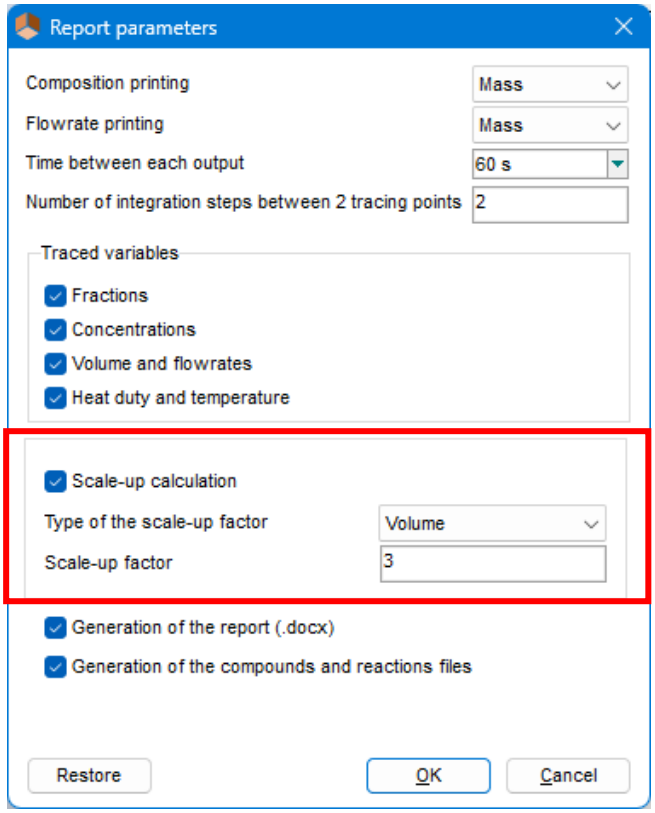


The minimum steam flow rate is the flow rate of steam required to perform the heat exchange with only the latent heat of vaporization of the steam (no sub-cooling). This value is greater than the one specified (200 kg/h). The “real” heat exchange coefficient is the one used in the calculation. The “theoretical” one is the one necessary to perform the heat exchange using the minimum value for the steam flow rate.



7.4. Scale-up

The objective is to perform batches three times bigger. The scale-up parameters are:



The scale-up techniques of a process are based on the principle of similarity. This principle states that the ratios between one or more parameters must be the same at both scales to reproduce the same phenomena and so to obtain a final product of the same quality. For a mechanically stirred tank, there are five principles:

- ✓ Geometric similarity,
- ✓ Kinematic similarity,
- ✓ Dynamic similarity,
- ✓ Thermal Similarity,
- ✓ Chemical similarity.

The scale-up of a mixing system is based on the principle of geometric similarity, *i.e.* on the conservation of dimension ratios between pilot and industrial scales:

$$k_{Linear} = \frac{T_{Industrial}}{T_{Pilot}} = \frac{D_{Industrial}}{D_{Pilot}} = \dots$$

As far as it's possible, the same type and the same geometry of agitator will be used. With the geometric similarity, the characteristics of the mixing device, *e.g.* the power number, are identical at both scales. But the modification of the volume of the tank induces a modification of the volume to surface ratio. The surface of the tank increases less than the volume. In this example, the volume is increased by a factor 3, but the surface is increased by a factor 2. This can be a problem for the heat transfer if it is done through the wall like in this example (external jacket). It happens then the geometric similarity can be no more maintained in such cases. BatchReactor can be used to

simulate the new scale and adapt, if necessary, the heat transfer device to maintain its performance (*e.g.* jacket width, baffled jacket, agitation nozzles…).

From the volume scale-up factor of 3, BatchReactor calculated the linear scale-up factor: 1.44. The following table (available in BatchReactor results) shows the size of the new vessel.

Vessel scale-up		
	Simulation	**Scale-up**
Bottom geometry	Torispherical	
Tank diameter (m)	1.40	2.02
Curve radius #1 (m)	1.40	2.02
Curve radius #2 (m)	0.14	0.20
Number of baffles (m)	4	
Maximum liquid height (m)	1.68	2.43
Maximum liquid volume (m)	2.45	7.34
Mixing device scale-up		
	Simulation	**Scale-up**
Impeller	3 retreating-blades impeller (steel)	
Diameter (m)	0.70	1.01
Off bottom height (m)	0.45	0.65

The impossibility to scale-up while respecting the dynamic similarity leads to choose a dimensionless number or a parameter whose influence is predominant on the phenomenon studied and which will be kept constant: it's the invariant. The choice of this invariant results from the knowledge of the process. Pilot tests are here very important. Keeping constant at both levels (pilot and industrial) an invariant induces a variation of the process parameters by a multiplicative factor linked to the extrapolation factor *k*. The main invariants and the main characteristics are considered in BatchReactor: tip velocity, Reynolds number, power per unit volume…

Note that the laminar flow cases have been established for a Newtonian fluid.

The table of the next page (provided by BatchReactor) gives this information for this simulation (scale-up by a factor 3 on volume). For example, if the rotational speed was kept constant between the two scales, the power in the case of a turbulent flow would be multiplied by a factor 6.

	Multiplicative factors affecting the characteristic quantites depending on the invariants											
Invariant	Constant	Rotational speed	Tip speed	Reynolds number	Froude number	Weber number	Power per unit volume		Power		Zwietering correlation	Usage rule
							Laminar	Turbulent	Laminar	Turbulent		
Rotational speed	N		1.4	2.1	1.4	3.0	1.0	2.1	3.0	6.2	1.4	1.3
Tip speed	ND	0.69		1.4	0.69	1.4	0.48	0.69	1.4	2.1	0.95	0.93
Reynolds number	ND^2	0.48	0.69		0.33	0.69	0.23	0.23	0.69	0.69	0.66	0.64
Froude number	N^2D	0.83	1.2	1.7		2.1	0.69	1.2	2.1	3.6	1.1	1.1
Weber number	N^2D^3	0.58	0.83	1.2	0.48		0.33	0.40	1.0	1.2	0.79	0.77
P/V laminar	N	1.0	1.4	2.1	1.4	3.0			3.0		1.4	1.3
P/V turbulent	N^3D^2	0.78	1.1	1.6	0.89	1.8				3.0	1.1	1.1
Power laminar	N^2D^3	0.58	0.83	1.2	0.48	1.0	0.33				0.79	0.77
Power turbulent	N^3D^5	0.54	0.78	1.1	0.43	0.89		0.33			0.74	0.73
Zwietering correlation	ND^0.85	0.73	1.1	1.5	0.77	1.6	0.54	0.82	1.6	2.5		0.98
Usage rule	ND^0.8	0.75	1.1	1.6	0.80	1.7	0.56	0.86	1.7	2.6	1.0	

For each operating step, BatchReactor indicates the Reynolds number and the corresponding flow regime: turbulent in both steps with Reynolds number around 10^6.

The same table is also available for each step. At this level, the value of each invariant (rotational speed, tip velocity, power per unit volume…) is shown. The following table is the one for the heating step of this example. For example:

- ✓ The tip velocity is about 3.3 m/s with the indication that this value is inside the usual range for this type of impeller (radial flow impeller).
- ✓ The power per unit volume is about 240 W/m^3 with the indication that this is a moderate level. This level is the usual one for thermal transfer and gas dispersion operation in an agitated tank. This is coherent with the application studied in this example.

In the same table the values reached by the parameters depending on the chosen invariant are displayed. The power per unit volume is one of the invariants which can be chosen in the case of gas-liquid reaction. In the table printed next page, one can see that keeping constant this invariant:

- ✓ The tip velocity increases slightly (3.7 m/s instead of 3.3 m/s) and remains in the usual operating range for a radial flow impeller.
- ✓ The flow inside the tank is still turbulent (Reynold number about 1.5x10^6).
- ✓ The power needed for the mixer is increased by a factor 3: 1.6 kW instead of 0.54 kW. This seems to be an acceptable power input.

Note that if no baffle was specified, BatchReactor would compute the depth of the vortex for the simulation and for the scale-up cases corresponding to each invariant.

			Values of the characteristic quantities at the industrial scale depending on the invariants							
Invariant	Unit	Simulation	Rotational speed (rpm)	Tip speed (m/s)	Reynolds number (-)	Froude number (-)	Weber number (-)	Power per unit volume (W/m3)	Power (kW)	Zwietering correlation (m^0.85/s)	Usage rule (m^0.85/s)
Rotational speed	(rpm)	90.		4.8 (correct)	1.92E+06	0.23	7.88E+04	5.00E+02 (moderate)	3.4	1.5	1.5
Tip speed	(m/s)	3.3 (correct)	62.		1.33E+06	0.11	3.79E+04	1.67E+02 (low)	1.1	1.0	1.0
Reynolds number	(-)	9.24E+05	43.	2.3 (low)		5.35E-02	1.82E+04	56. (low)	0.38	0.73	0.73
Froude number	(-)	0.16	75.	4.0 (correct)	1.60E+06		5.46E+04	2.88E+02 (moderate)	2.0	1.3	1.3
Weber number	(-)	2.63E+04	52.	2.7 (low)	1.11E+06	7.72E-02		96. (low)	0.65	0.87	0.87
Power per unit volume	(W/m3)	2.40E+02 (moderate)	71.	3.7 (correct)	1.51E+06	0.14	4.83E+04		1.6	1.2	1.2
Power	(kW)	0.54	49.	2.6 (low)	1.04E+06	6.83E-02	2.32E+04	80. (low)		0.82	0.82
Zwietering correlation	(m^0.85/s)	1.1	66.	3.5 (correct)	1.41E+06	0.12	4.23E+04	1.96E+02 (low)	1.3		1.1
Usage rule	(m^0.8/s)	1.1	67.	3.5 (correct)	1.43E+06	0.13	4.38E+04	2.07E+02 (moderate)	1.4	1.1	

BatchReactor provides also indications on the scale-up of gas feeds. Two are presents in this example: one for the inert (nitrogen) and one for the reactant (chlorine). For gas feeds, two scale-up criteria are generally considered: the superficial gas velocity and the vvm (volume gas flow rate per volume of liquid). This last one is usually considered for scale-up of gas-liquid reactions. The following table shows the results for the reactant feed in the reaction step of the present example. The scale-up at constant superficial velocity leads to a new gas flow rate slightly lower than the one obtained with a scale-up at constant vvm.

The scale-up of the gas sparger must also be careful. Attention must be focused on the location of the gas sparger relative to the agitator and the tank wall and bottom, on the number of holes and on their diameter.

Once the new gas flow rate selected, it can be interesting to check that the gas dispersion is still in the loading or the complete dispersion regime to allow a good repartition of the gas in the tank and a good working of the impeller. Analyzing the evolution of the power required when the gas is injected in the tank is also interesting. A high drop of the power consumption when the gas is present in the tank can indicate a flooding of the agitator.

			Scale-up at	
	Unit	Simulation	Constant us	Constant vvm
Gas flow rate	(m3/h)	7.0	15.	21.
Superficial velocity (us)	(m/s)	1.26E-03		1.82E-03
vvm flow rate (vvm)	(1/min)	4.89E-02	3.39E-02	

More information about scale-up can be found in [XUE06], [KRE16].

8. REFERENCES

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[REN68] RENON H., J.M. PRAUSNITZ, “Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures”, AIChE J., 14(3), 135-144 (1968)

[ROW23] 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 (2023)

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9. NOMENCLATURE

C_{Ai}	Concentration of the compound A for the reaction i	mol/l
C_{Bi}	Concentration of the compound A for the reaction i	mol/l
D	Agitator diameter	m
Ea_i	Activation energy of the reaction Ri	J/mol
K	Scale-up factor	(-)
k_i	Pre-exponential factor of the reaction Ri	l/(mol.s)
R	Perfect gas constant	J/(mol.K)
r_i	Rate of the reaction i	mol/(l.s)
t	Temperature	K
T	Tank diameter	m

Subscript

Industrial	Relative to the industrial scale
Linear	Relative to 2D length
Pilot	Relative to the pilot scale