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BATCHREACTOR APPLICATION EXAMPLE

REACTOR WITH HETEROGENEOUS CATALYTIC REACTIONS

EXAMPLE PURPOSE
The main interest of this example is the simulation of a set of three heterogeneous catalytic reactions. These reactions follow the Langmuir-Hinshelwood formalism.

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CORRESPONDING BATCHREACTOR FILE	*BATCHREA_EX_EN-Langmuir-reactions.pbpr*

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1. INTRODUCTION

The reaction scheme is made up with three heterogeneous catalytic reactions, some of them consecutive, others parallel. The Langmuir-Hinshelwood formalism is used to model the kinetic rate laws. The solvent used is n-dodecane.

2. REACTION MECHANISM

The synthesis reaction of B_IV from A_IV is the main reaction (R1). It is a reversible reaction but not at equilibrium. The secondary reaction (R2) degrades B_IV into C_IV. The last reaction (R3) consumes A_IV reactant to form D_IV at the expense of the desired product B_IV.

$$A\_IV \overset{(R1)}{\Longleftrightarrow} B\_IV \overset{(R2)}{\Longrightarrow} C\_IV$$

$$A\_IV \overset{(R3)}{\Longrightarrow} D\_IV$$

3. COMPONENTS

The components taken into account in the simulation appear in the table below:

Name	CAS number[1]
A_IV	55000-01-6
B_IV	55000-02-7
C_IV	55000-03-8
D_IV	55000-04-5
n-dodecane(*)	112-40-3

The component with an asterisk is 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 [ROW23].

The other compounds have been created using the **Clone this compound** functionality in Simulis Thermodynamics. The reactant A_IV is assimilated to benzyl alcohol (CAS number[1]: 100-51-6), the desired product B_IV to o-cresol (CAS number[1]: 95-48-7) and the secondary products C_IV and D_IV are respectively assimilated to m-cresol (CAS number: 108-39-4) and p-cresol (CAS number1: 106-44-5). Only the specific names and the CAS numbers[1] (arbitrary number) have been modified relating to the components taken from the database.

[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 reactor is modelled as a single-phase liquid reactor (§ 7), therefore no vapor-liquid equilibrium is taken into account. The **Ideal** thermodynamic profile is then selected in Simulis Thermodynamics.

5. REACTION MATHEMATICAL MODEL

The kinetics of transformation of A_IV into B_IV (R1) is modelled by the following Langmuir-Hinshelwood rate law:

$$r_1 = \frac{k_1 exp\left(-\frac{Ea_1}{RT}\right)\left([A\_IV] - \frac{[B\_IV]}{K_1}\right)}{\left(1 + K_{A\_IV}[A\_IV] + K_{B\_IV}[B\_IV]\right)^1}$$

The kinetics of transformation of B_IV into C_IV (R2) is modelled by the following Langmuir-Hinshelwood rate law:

$$r_2 = \frac{k_2 exp\left(-\frac{Ea_2}{RT}\right)[B\_IV]}{\left(1 + K_{A\_IV}[A\_IV] + K_{B\_IV}[B\_IV]\right)^1}$$

The kinetics of transformation of A_IV into D_IV (R3) is modelled by the following Langmuir-Hinshelwood rate law:

$$r_3 = \frac{k_3 exp\left(-\frac{Ea_3}{RT}\right)[A\_IV]}{\left(1 + K_{A\_IV}[A\_IV] + K_{B\_IV}[B\_IV]\right)^1}$$

The following table shows the reactions parameters.

Reaction	k_i (s^{-1})	Ea_i (cal/mol)	K_i (-)
(R1)	1 738,15	6 706	$K_1 = exp\left(-12{,}3245 + \frac{5412{,}427}{T}\right)$
(R2)	5,977	4 672	-
(R3)	174 048	13 442,8	-

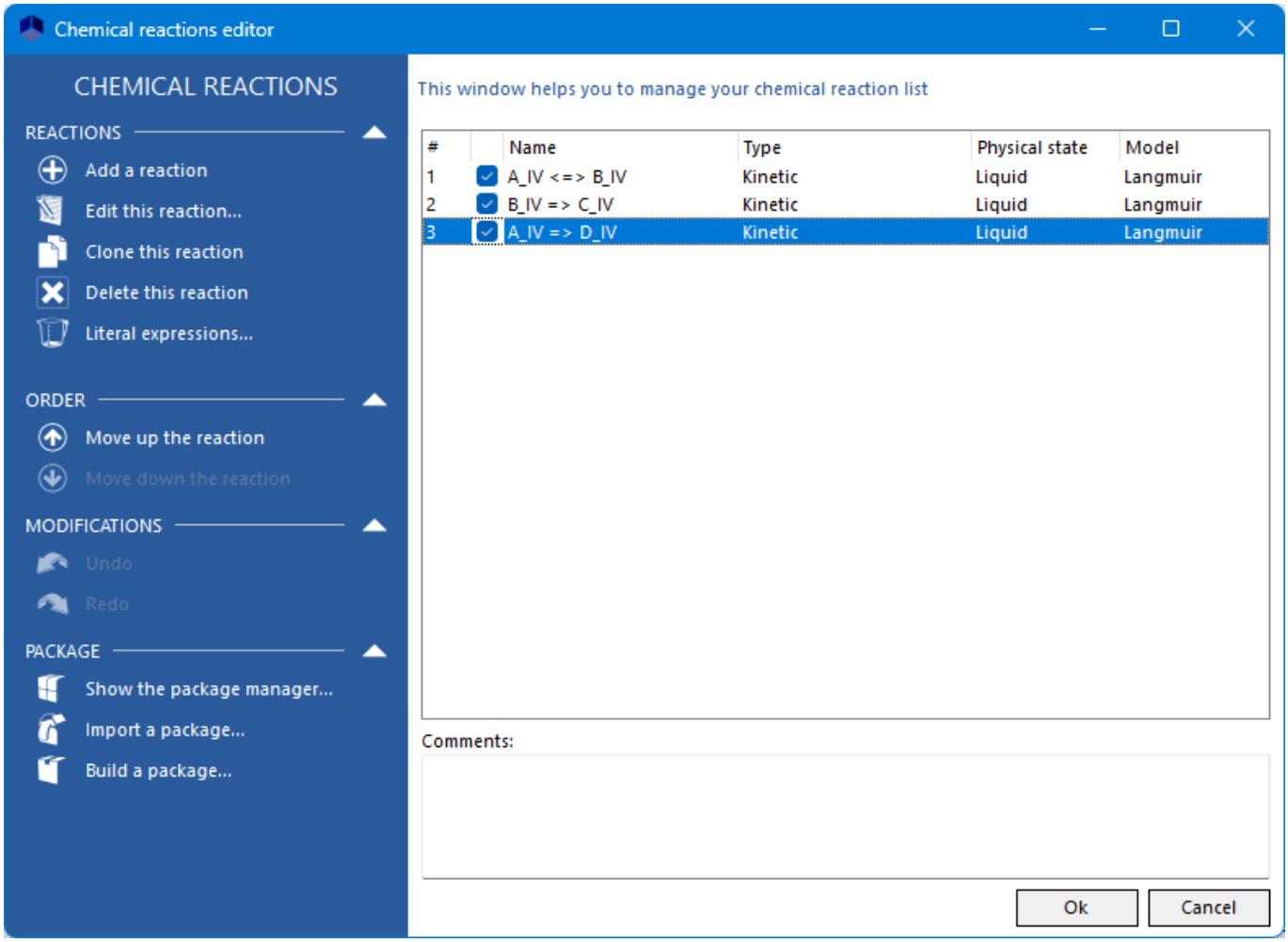
The adsorption constants are expressed as follows:

$$K_{A\_IV} = 1{,}76643.10^{-5} exp\left(\frac{8365{,}2\ cal/mol}{RT}\right)$$

$$K_{B\_IV} = 1{,}704239.10^{-3} exp\left(\frac{4780{,}15\ cal/mol}{RT}\right)$$

6. REACTION MODEL IMPLEMENTATION USING SIMULIS REACTIONS

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



These three reactions follow the Langmuir-Hinshelwood formalism. They are then described in the standard interface of Simulis Reactions.

All the reactions take place in liquid phase.

The heat of reaction of each reaction is calculated using the standard enthalpies of formation.

7. SIMULATION

7.1. Process description

7.1.1. Reactor

The reactor modelled for the implantation of this synthesis is a single-phase liquid reactor. No heating/cooling system has been described. The heat duty necessary to maintain the reactor isothermal will be calculated by BatchReactor. The reactant, the solvent and the catalyst are present in the initial load; there is no feed.

The initial conditions appear in the table below:

Initial conditions	
Temperature	60°C
Pressure	1 atm
Initial load	
Total weight	100 kg
A_IV	50% pds.
n-dodecane	50% pds.

The alarms are as follows:

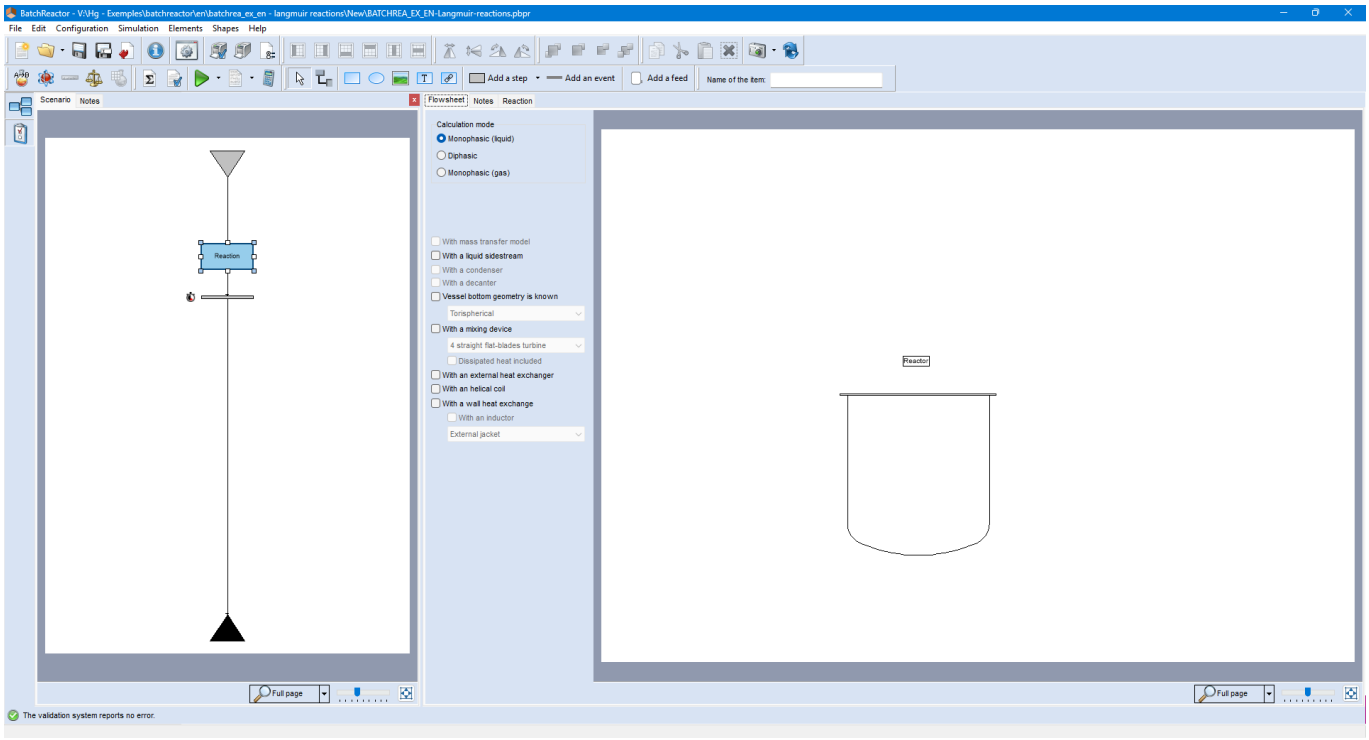
	Volume	**Temperature**
Minimum	1 l	0°C
Maximum	1 000 l	100°C

7.1.2. Operating mode

The operating mode is made up with a single step of isothermal reaction. The parameters appear in the following table:

Parameter	Step
Type	Specified reactor temperature
Reactor temperature	60°C
Reactor pressure	1 atm
Stop event	Time elapsed since the beginning of the step = 1 h

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

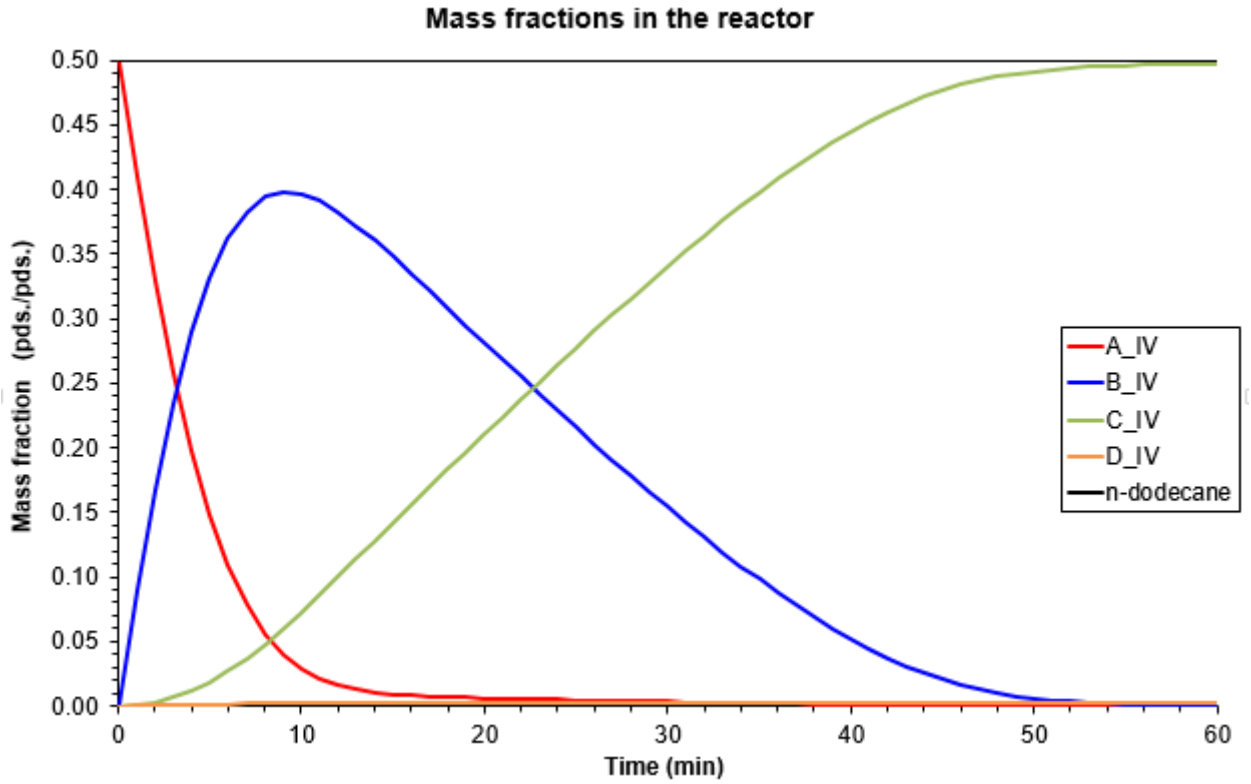


7.2. “Tips”

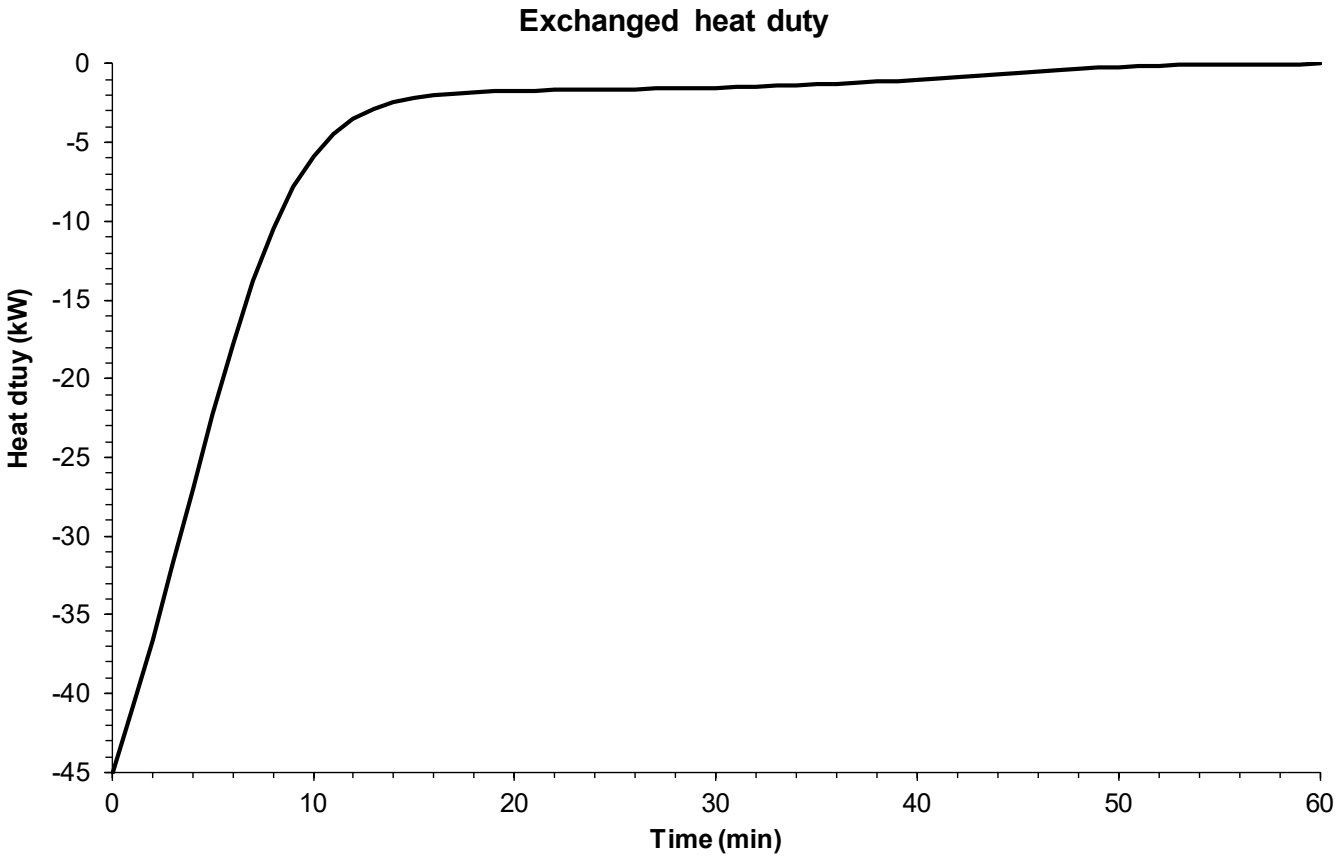
To get “smoother” profiles, the time interval between each output can be reduced to 60 s (instead of the default value fixed to 600 s), in the **Report parameters** window.

7.3. Results

The following graph shows the evolution of the mass fractions in the reactor. The content of A_IV decreases as it is consumed by two reactions: the synthesis of B_IV (R1) and D_IV (R3). The reversible reaction of B_IV to A_IV does not compensate its consumption. The content of B_IV increases as long as its production by the reaction (R1) is higher than its consumption by the reaction (R2), then it decreases showing thus a maximum. The content of C_IV only increases as it is produced only by the degradation of B_IV (R2). The content of D_IV also shows a maximum: growth as long as A_IV is present then decrease due to the slowdown of the production (R3) by depletion of A_IV. The reaction (R3) remains minor in this synthesis.



The following graph shows the evolution of the heat to remove in order to maintain the isothermal operation of the reactor at the temperature of 60°C. It decreases when the production of B_IV decreases.



8. REFERENCES

[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)

9. NOMENCLATURE

$[i]$	Concentration of the component i	mol.l^{-1}
Ea_i	Activation energy of reaction r_i	cal/mol
k_i	Pre-exponential factor of reaction r_i	s^{-1}
K_{A_IV}	Adsorption constant of A_IV	l.mol^{-1}
K_{B_IV}	Adsorption constant du B_IV	l.mol^{-1}
K_i	Equilibrium constant of reaction r_i	(-)
R	Perfect gas constant	cal.mol^{-1}.K^{-1}
r_i	Rate of reaction i	mol.l^{-1}.s^{-1}
T	Temperature	K