**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.

**ACCESS**

- [x] Free-internet
- [ ] Restricted to ProSim clients
- [ ] Restricted
- [ ] Confidential

**BATCHREACTOR CORRESPONDING FILE**

`BATCHREA_EX_EN-Langmuir-reactions.pbpr`
# TABLE OF CONTENTS

1. **INTRODUCTION** 3
2. **REACTION MECHANISM** 3
3. **COMPONENTS** 3
4. **THERMODYNAMIC MODEL** 4
5. **REACTION MATHEMATICAL MODEL** 4
6. **REACTION MODEL IMPLEMENTATION USING SIMULIS REACTIONS** 5
7. **SIMULATION** 6
   7.1. Process description 6
       7.1.1. Reactor 6
       7.1.2. Operating mode 7
    7.2. « Tips » 7
    7.3. Results 8
8. **REFERENCES** 10
9. **NOMENCLATURE** 11
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 $\text{B}_{\text{IV}}$ from $\text{A}_{\text{IV}}$ is the main reaction (R1). It is a reversible reaction but not at equilibrium. The secondary reaction (R2) degrades $\text{B}_{\text{IV}}$ into $\text{C}_{\text{IV}}$. The last reaction (R3) consumes $\text{A}_{\text{IV}}$ reactant to form $\text{D}_{\text{IV}}$ at the expense of the desired product $\text{B}_{\text{IV}}$.

\[
\text{A}_{\text{IV}} \overset{(R1)}{\rightleftharpoons} \text{B}_{\text{IV}} \overset{(R2)}{\rightarrow} \text{C}_{\text{IV}} \\
\text{A}_{\text{IV}} \overset{(R3)}{\rightarrow} \text{D}_{\text{IV}}
\]

3. COMPONENTS

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

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{A}_{\text{IV}}$</td>
<td>55000-01-6</td>
</tr>
<tr>
<td>$\text{B}_{\text{IV}}$</td>
<td>55000-02-7</td>
</tr>
<tr>
<td>$\text{C}_{\text{IV}}$</td>
<td>55000-03-8</td>
</tr>
<tr>
<td>$\text{D}_{\text{IV}}$</td>
<td>55000-04-5</td>
</tr>
<tr>
<td>n-dodecane(*)</td>
<td>112-40-3</td>
</tr>
</tbody>
</table>

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 [ROW17].

The other compounds have been created using the **Clone this compound** functionality in Simulis Thermodynamics. The reactant $\text{A}_{\text{IV}}$ is assimilated to benzyl alcohol (CAS number: 100-51-6), the desired product $\text{B}_{\text{IV}}$ to o-cresol (CAS number: 95-48-7) and the secondary products $\text{C}_{\text{IV}}$ and $\text{D}_{\text{IV}}$ are respectively assimilated to m-cresol (CAS number: 108-39-4) and p-cresol (CAS number: 106-44-5). Only the specific names and the CAS numbers (arbitrary number) have been modified relating to the components taken from the database.
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:

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

The kinetics of transformation of B\_IV into C\_IV (R2) is modelled by the following Langmuir-Hinshelwood rate law:

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

The kinetics of transformation of A\_IV into D\_IV (R3) is modelled by the following Langmuir-Hinshelwood rate law:

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

The following table shows the reactions parameters.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(k_i) (s(^{-1}))</th>
<th>(Ea_i) (cal/mol)</th>
<th>(K_i) (()</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>1 738,15</td>
<td>6 706</td>
<td>(K_1 = \exp\left(-12.3245 + \frac{5412.427}{T}\right))</td>
</tr>
<tr>
<td>(R2)</td>
<td>5,977</td>
<td>4 672</td>
<td>-</td>
</tr>
<tr>
<td>(R3)</td>
<td>174 048</td>
<td>13 442,8</td>
<td>-</td>
</tr>
</tbody>
</table>

The adsorption constants are expressed as follows:

\[
    K_{A\_IV} = 1,76643\times10^{-5}\exp\left(\frac{8365,2\ \text{cal/mol}}{RT}\right)
\]

\[
    K_{B\_IV} = 1,704239\times10^{-3}\exp\left(\frac{4780,15\ \text{cal/mol}}{RT}\right)
\]
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 computed using the standard enthalpies of formation (1 atm, 25°C, perfect gas).
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:

<table>
<thead>
<tr>
<th>Initial conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total weight</td>
</tr>
<tr>
<td>A_IV</td>
</tr>
<tr>
<td>n-dodecane</td>
</tr>
</tbody>
</table>

The alarms are as follows:

<table>
<thead>
<tr>
<th>Volume</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>1 l</td>
</tr>
<tr>
<td>Maximum</td>
<td>1 000 l</td>
</tr>
<tr>
<td></td>
<td>0°C</td>
</tr>
<tr>
<td></td>
<td>100°C</td>
</tr>
</tbody>
</table>
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:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Specified TR without thermal device</td>
</tr>
<tr>
<td>Reactor temperature</td>
<td>60°C</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Stop event</td>
<td>Time elapsed since the beginning of the step = 1 h</td>
</tr>
</tbody>
</table>

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

![Screenshot of the scenario and flowsheet](image)

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

9. NOMENCLATURE

\[ [i] \quad \text{Concentration of the component } i \quad \text{mol.l}^{-1} \]
\[ E_{A_i} \quad \text{Activation energy of reaction } r_i \quad \text{cal/mol} \]
\[ k_i \quad \text{Pre-exponential factor of reaction } r_i \quad \text{s}^{-1} \]
\[ K_{A_{IV}} \quad \text{Adsorption constant of A_{IV}} \quad \text{l.mol}^{-1} \]
\[ K_{B_{IV}} \quad \text{Adsorption constant du B_{IV}} \quad \text{l.mol}^{-1} \]
\[ K_i \quad \text{Equilibrium constant of reaction } r_i \quad (-) \]
\[ R \quad \text{Perfect gas constant} \quad \text{cal.mol}^{-1}.\text{K}^{-1} \]
\[ r_i \quad \text{Rate of reaction } i \quad \text{mol.l}^{-1}.\text{s}^{-1} \]
\[ T \quad \text{Temperature} \quad \text{K} \]