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SIMULIS KINETICS APPLICATION EXAMPLE

IDENTIFICATION OF THE REACTION SCHEME OF THE THYMOL SYNTHESIS

EXAMPLE PURPOSE
This example presents the use of experimental concentration data to identify the kinetic parameters of a reaction scheme. The reactions taken into account are controlled by kinetics. At the end of the identification, a reactive calculator is generated. This way, the components, the thermodynamic model and the chemical reactions can be easily loaded in BatchReactor and BatchColumn simulations.

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CORRESPONDING SIMULIS KINETICS FILE	*SIMKIN_EX_EN-Thymol.kin*

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.

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1. INTRODUCTION

Thymol is a phenol contained in the thyme oil and in the volatile essential oils of other plants. It takes the form of colorless crystals with a specific aromatic smell. It is soluble in alcohols, in fat and oil, but slightly soluble in water. It is notably used for its antiseptic action, its antibacterial properties and its antifungal effect, as well as to stabilize the pharmaceutical preparations.

This example deals with the identification of the kinetic parameters of the thymol synthesis (reaction scheme is made of one main reaction and three side reactions). The experimental data are supplied in concentration.

It is the first example of a series of three examples dealing with the synthesis and the purification of thymol. The second example “BATCHREA_EX_EN – Thymol” studies the synthesis of thymol in a batch reactor using the kinetics identified in this example. The third example “BATCHCOL_EX_EN – Thymol” deals with the thymol purification by batch distillation after the synthesis.

2. REACTION MECHANISM

The main chemical reaction for the thymol synthesis from m-cresol is as follows:

$$m\text{–}\,cresol + propylene \rightarrow thymol$$

Namely:

$$C_7H_8O + C_3H_6 \rightarrow C_{10}H_{14}O \quad \text{(R1)}$$

Three competing reactions are taken into account:

- ✓ 3M2P synthesis:

$$m\text{–}\,cresol + propylene \rightarrow 3M2P$$

Namely:

$$C_7H_8O + C_3H_6 \rightarrow C_{10}H_{14}O \quad \text{(R2)}$$

- ✓ 3M5P synthesis:

$$m\text{-}cresol + propylene \rightarrow 3M5P$$

Namely:

$$C_7H_8O + C_3H_6 \rightarrow C_{10}H_{14}O \quad \text{(R3)}$$

- ✓ 3M4P synthesis:

$$m\text{–}\,cresol + propylene \rightarrow 3M4P$$

Namely:

$$C_7H_8O + C_3H_6 \rightarrow C_{10}H_{14}O \quad \text{(R4)}$$

3. COMPONENTS

The components taken into account in the kinetic parameters identification are the following ones:

Name	Formula	CAS Number[1]
Propylene(*)	C_3H_6	115-07-1
m-cresol(*)	C_7H_8O	108-39-4
Thymol(*)	$C_{10}H_{14}O$	89-83-8
3-methyl-2-isopropylphenol (3M2P)	$C_{10}H_{14}O$	-
1-methyl-3-hydroxy-5-isopropyl benzene (3M5P)(*)	$C_{10}H_{14}O$	3228-03-3
1-methyl-3-hydroxy-6-isopropyl benzene (3M4P)(*)	$C_{10}H_{14}O$	3228-02-2

Components with an asterisk are taken from the standard database of Simulis Thermodynamics, thermodynamics server used in Simulis Kinetics. The thermophysical properties stored in this database are the DIPPR recommended values [ROW23].

The 3M2P component (3-methyl-2-isopropylphenol) has been created by cloning the thymol component from the standard database. Only the name, the CAS number[1], the normal boiling point and the vapor pressure have been modified:

- ✓ IUPAC name: 3M2P
- ✓ Specific name: 3-methyl-2-isopropylphenol
- ✓ CAS Number[1]: 55000-01-6 (arbitrary number)
- ✓ Normal boiling point: 501,1 K
- ✓ Vapor pressure:
  - Correlation : Equation #99
  - T_{min} : 50 K
  - T_{max} : 700 K

$$Ln(P^0) = 20{,}88 - \frac{7569}{T + 30{,}15}$$

In order to display the components acronyms in the interface instead of their full name in the standard database, the 3M2P, 3M4P and 3M5P acronyms are specified as “IUPAC name” of the corresponding components. This way, the names defined can be kept in **Specific name**.

4. THERMODYNAMIC MODEL

In this example, the **Ideal** thermodynamic profile has been chosen.

[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.*

5. IDENTIFICATIONS

5.1. Parameters

5.1.1. Reactions

For all the reactions described in paragraph 2:

- ✓ Order 1 with respect to the reactants,
- ✓ Order 0 with respect to the products.

5.1.2. Parameters to identify

For each reaction described in paragraph 2, the parameters to identify are the following ones:

- ✓ Pre-exponential factor,
- ✓ Activation energy of the reaction.

5.1.3. Experimental data

The following table specifies the experimental operating data.

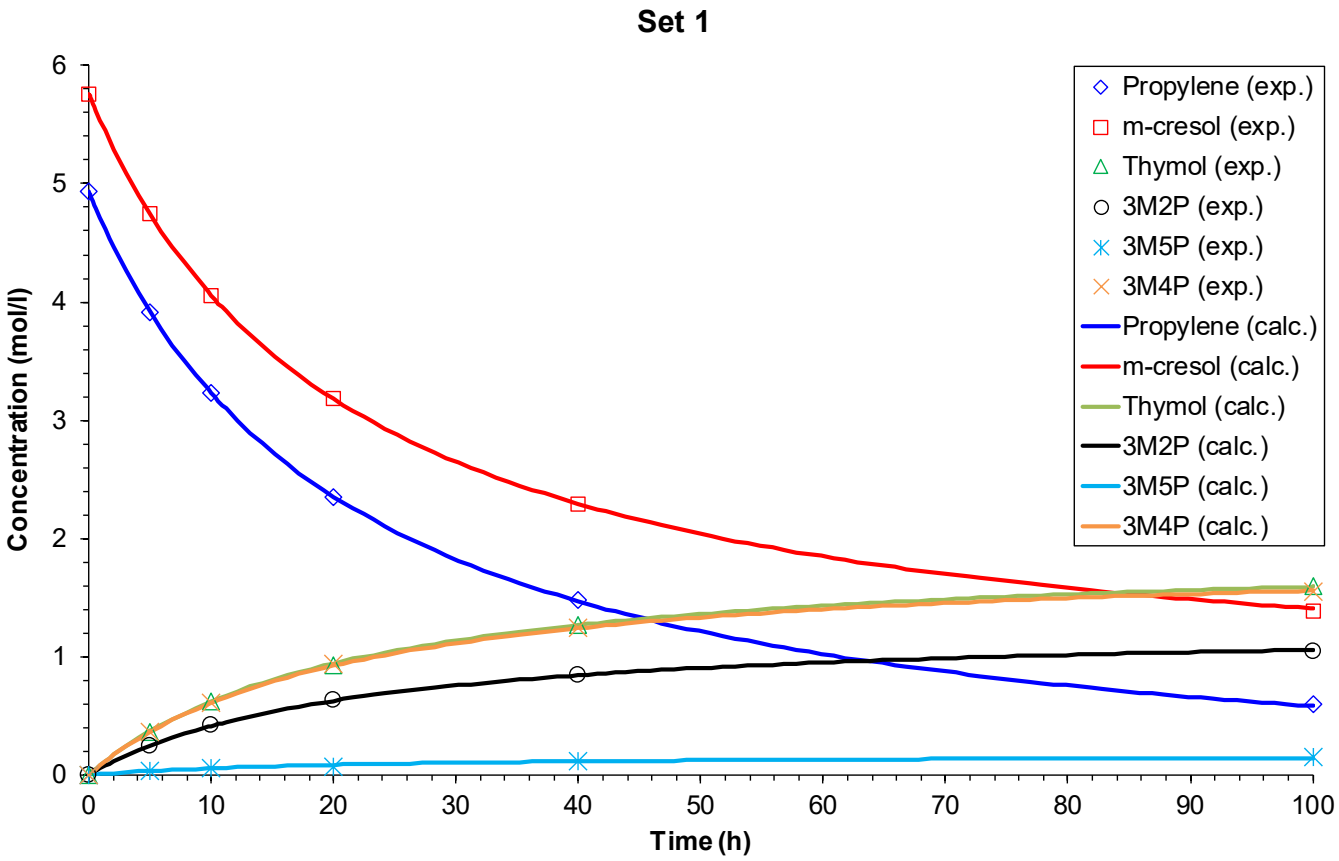
	Set 1	**Set 2**
Isothermal data	Yes	
Volume	constant	
Initial conditions		
Temperature	15°C	35°C
Pressure	1 atm	1 atm
Volume	1 l	1 l
Composition		
Propylene	4,9338 mol/l	4,7526 mol/l
m-cresol	5,7597 mol/l	5,5481 mol/l
Reaction duration	from 0 h to 100 h	
Experimental data file		
Name	Thymol_Set1.txt	Thymol_Set2.txt
Time unit	h	
Concentration unit	mol/l	
Data order	Time, [m-cresol], [Thymol], [3M2P], [3M5P], [3M4P], [Propylene]	

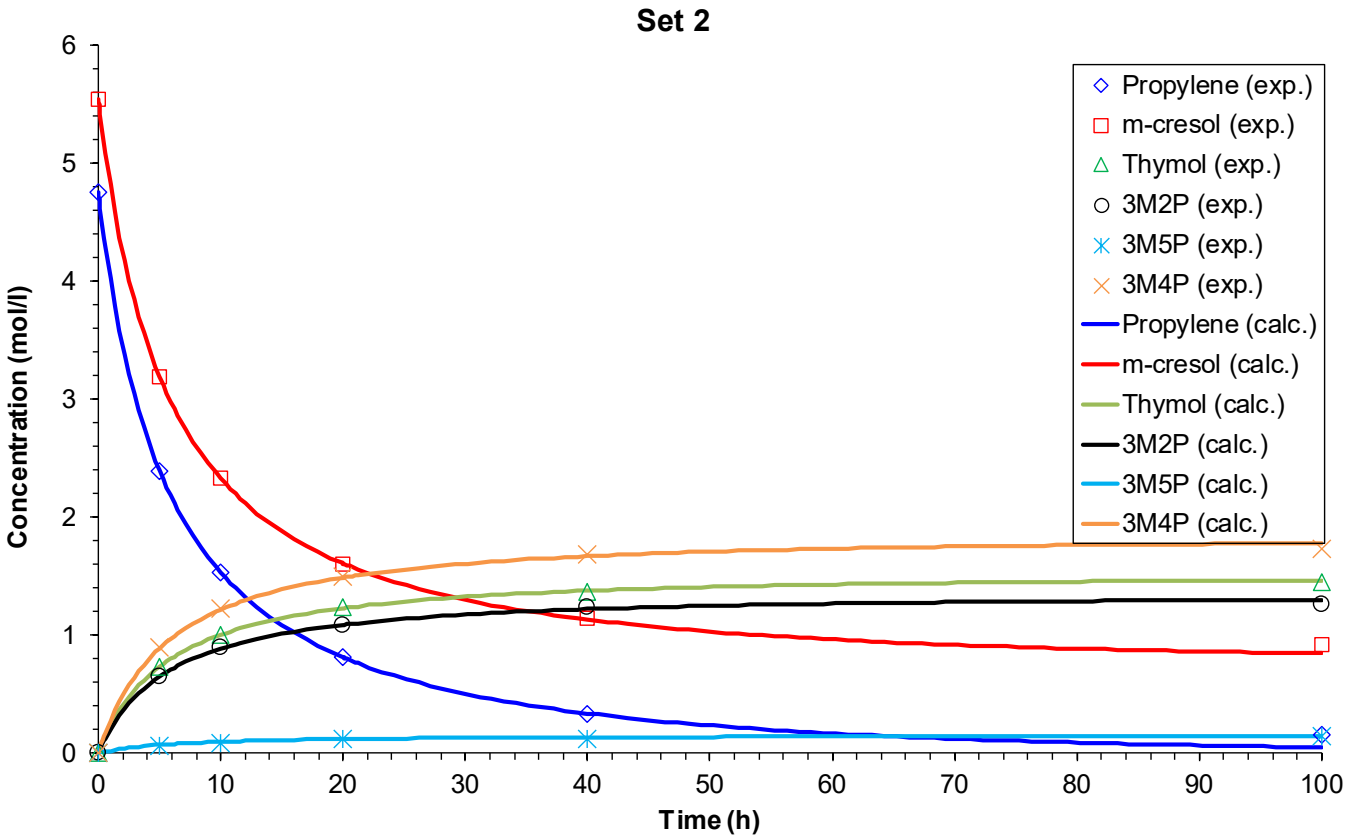
5.2. Results

The following table shows the values of the parameters identified as well as their confidence interval.

	Pre-exponential factor ($l.mol^{-1}.h^{-1}$)	Activation energy (cal/mol)
Thymol synthesis	$1{,}9710^{5}$ +/- 3.10^{-2}	10 266 +/- 2.10^{-2}
3M2P synthesis	$1{,}11.10^{7}$ +/- 3.10^{-2}	12 806 +/- 2.10^{-2}
3M5P synthesis	$7{,}46.10^{4}$ +/- 2.10^{-1}	11 082 +/- 2.10^{-1}
3M4P synthesis	$5{,}18.10^{6}$ +/- 3.10^{-2}	12 149 +/- 2.10^{-2}

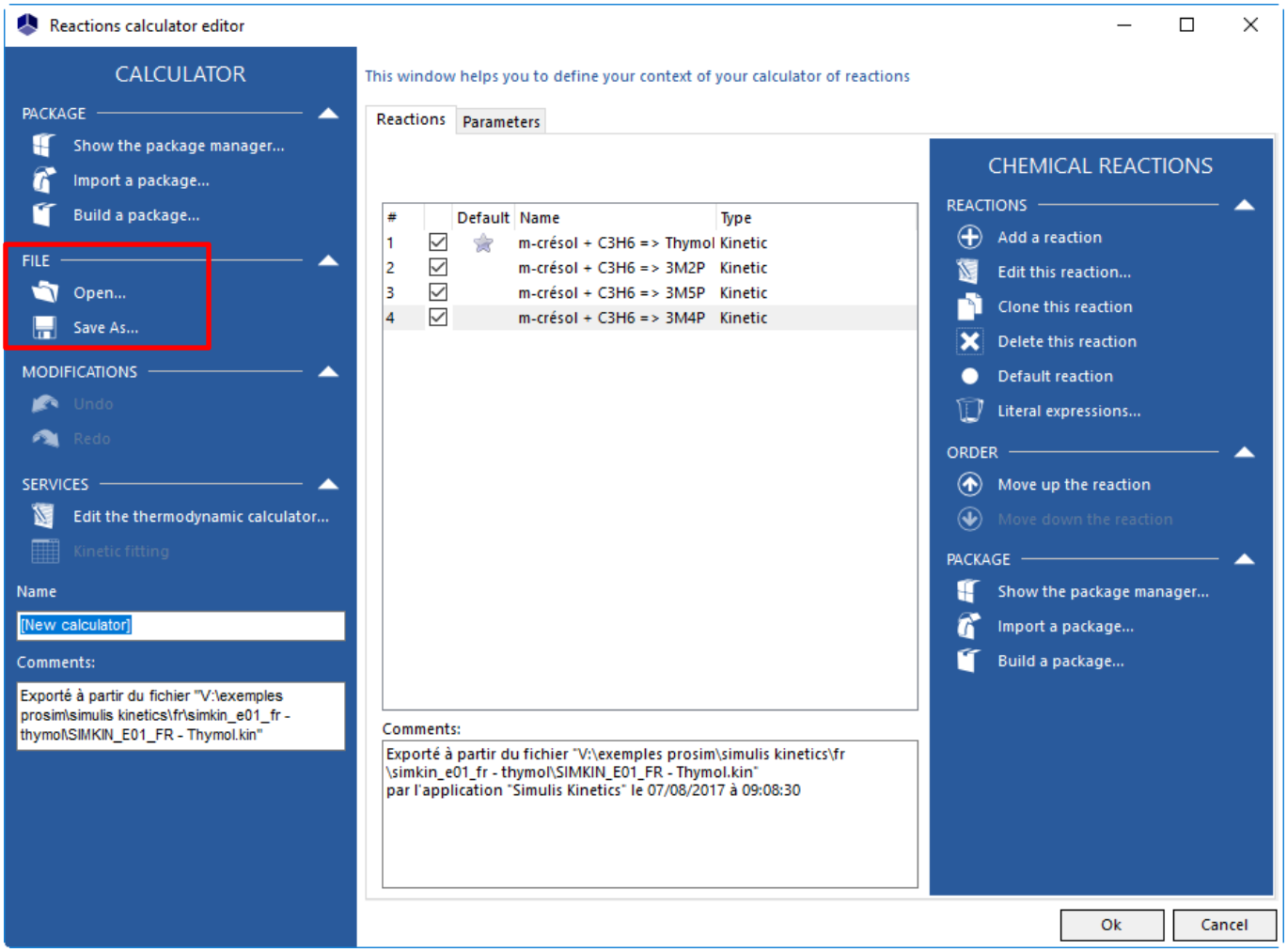
The following figures show a comparison between the experimental data and the identified models.





6. RESULTS EXPORT

Click this icon  to export the components, the thermodynamic model, the reactions and their parameters to a ".ReacCalculator" file from the **File/Save as** menu in the window that opens. This way, it will be possible to reload the information when implementing the simulation files in BatchReactor and BatchColumn.



7. 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)

8. NOMENCLATURE

$[i]$	Concentration of the compound i	mol/l
P^0	Vapor pressure of 3M2P	mmHg
T	Temperature	K

Indices

Min	Minimum value
Max	Maximum value