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KBR (Kinetics in Batch Reactors): a MATLAB-based application with a friendly Graphical User Interface for chemical kinetic model simulation and parameter estimation

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ABSTRACT

The simulation of chemical kinetic models is necessary in order to analyze comprehensive chemical reaction mechanisms and perform the estimation of the kinetic parameters. In many cases, a chemical process can be composed of several series and/or independent reactions that requires a complex set of kinetic equations to be solved. Computer-based tools for the study of kinetics of chemical reaction networks have been used since the last 50 years. However, the educational tools in this field should be friendly for the user and easy to learn and adapt to practical cases, avoiding long frustrating learning curves. Herein, the main objective of this contribution is to present a Matlab® application for the evaluation of Kinetics in Batch Reactors (*KBR*), which will help students to estimate kinetic parameters of complex chemical reaction models. The *KBR* application was used in the Final Degree Projects of Chemical Engineering and Environmental Engineering Degrees at Rey Juan Carlos University (Spain). This application provides a friendly Graphical User Interface to formulate any kind of kinetic model for subsequent simulation in order to monitor the evolution of reagents and products along the reaction time. Moreover, the student will be able to estimate kinetic parameters according to available experimental data as well as to apply sensitivity analysis of those parameters for particular cases of chemical reactions in batch systems. Finally, the results can be exported for further analysis as a spreadsheet of an Excel® file (.xlsx).

1. Introduction

The understanding of kinetic reaction principles occurring in a simple batch reactor is mandatory in the academic learning of graduates in Chemical Engineering. Chemical kineticsćalculations on simple systems of one or two reactions often have an easy analytical solution. Thus, the evolution of the concentration of the reagent and product in the case of first order reactions (A→B) can be determined from known values of initial reagent's concentration and the reaction rate constant. However, more complex chemical reaction networks implies the increase of kinetic equations and parameters based on more complex models, including series or independent chemical reactions for homogeneous systems or even heterogeneous chemical reaction models (Sandu and Sander, 2006; Huang and Liu, 2015). Computer simulations have been used since 1970 to understand complex chemical kinetic models and principles (Bigger, 2011), producing a significant impact especially in chemical engineering education (Cartaxo et al., 2014; Hernández et al., 2014; Golman, 2016). The advantages of chemical engineering simulations have been widely established in literature, as this practice can reduce the cost of laboratory facilities, increase the number of experiments in the learning process or make possible to study processes that involve dangerous materials or conditions (Skorzinski et al., 2009).

The simulation and analysis of comprehensive chemical reaction models and parameter estimation require the development of efficient tools for the computational simulation of chemical kinetic systems. Sometimes, the set of kinetic equations are inherently difficult to operate and may require specialized software to be fully solved (Morgenroth et al., 2002; Manafov, 2015). Commercially available simulation software, such as Matlab, Mathematica or Python (Brenner et al., 2005; Ibrahim, 2011; Li and Huang, 2017) or dedicated simulation software, such as CHEMSIMUL (Kirkegaard and Ejegbakke, 2000) or CHEMKIN (Coltrin et al., 2001) can deal with the required calculations.

The use of Matlab-like applications is a challenging task in chemical engineering education due to the mathematics-intensive properties of computational modeling methods (Li and Huang,

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2017). Currently, several studies have revealed that chemical engineering students have scarce knowledge of Matlab programming, as they studied it in a basic and disciplinary neutral level, mostly in the first course of the degree (Wong and Barford, 2010; Teles dos Santos et al., 2018). Consequently, they are not usually able to implement their programming skills on solving real systems related to chemical engineering in the following courses. In this sense, the induction course should be accompanied to a process of getting to know how to use programming skills in several matters, like reaction engineering, in order to avoid an insurmountable obstacle (Dry et al., 2016).

On the other hand, dedicated simulation packages are designed to simulate only specific engineering problems (Aspen plus® or Aspen HYSYS® from Aspentech), obtaining results quickly, but they are also usually expensive and the source code is not available, so it is not possible to modify or upgrade the simulation package easily (Ibrahim, 2011). Additionally, one potential barrier for teaching using dedicated software is the reluctance of academics to learn how to use a new and complex software (Dahm et al., 2002; Belton, 2016). Therefore, there is a need to develop alternative educational applications to help students learning the theoretical principles by performance of practical simulations and visualization of the results (Golman, 2016). In this sense, a good kinetic simulator should provide an effective tool for studying a set of reactions without the need of programming skills from the student's side. This simulator application should be able to simulate the reaction progress by specifying the reaction stoichiometry and rate constants, as well as the initial conditions of all chemical species. However, students may be warned that a kinetic simulator cannot guarantee a correct answer to any set of reactions (Durruty and Ayude, 2014), and they should be able to make a critical analysis of the results.

In this work, we present the *KBR* (Kinetics in Batch Reactor) application, a Matlab® code aimed to construct kinetic models. The *KBR* code uses a friendly Graphical User Interface (GUI) to control all the options of the application. This *KBR* application can be used for the simulation of a simple chemical reaction to complex chemical reaction networks, including series and independent reactions for homogeneous batch reactors or heterogeneous catalytic mechanisms. With this application, students will be able to observe the evolution of the chemical species presented in the reaction media along the reaction time. Additionally, the students will perform the model's parameter estimation according to the experimental data obtained in batch experiments, as well as the sensitivity analysis of those parameters. The results can be easily saved for further analysis as a spreadsheet of an Excel© file (".xlsx"). The main benefits for the students derived from the use of the *KBR* application can be summarized as follows: i) analysis of physical and chemical phenomena involved in simple and complex chemical reaction networks; ii) development of their own mathematical models; iii) kinetic parameters estimation; and iv) sensitivity analysis for critical variables. This Matlab-based application for Kinetics in Batch Reactors was tested by several students for the performance of Final Degree Projects in Chemical Engineering and Environmental Engineering Degrees at Universidad Rey Juan Carlos (Madrid, Spain).

2. Simulation of chemical processes in *KBR*

To define any kinetic model using the *KBR* application, the following steps should be executed:

1 Identification of components (chemical compounds of the reactions, C_j).
2 Identification of the reactions (p_i).
3 Formulation of the kinetic rate equation for each reaction (r_{pi}).
4 Correlation of the reaction equations with the stoichiometric coefficients of the components ($k_{pi,Cj}$) for each reaction.

Table 1
Stoichiometry matrix of multiple reactions for simulation in *KBR*.

Reaction (*i*)	Components (*j*)				Kinetic rate equation of reaction (i)
	C_1	C_2	C_3	$C_{j...}$	
p_1	$k_{p1,C1}$	$k_{p1,C2}$	$k_{p1,C3}$	$k_{p1,Cj}$	r_{p1}
p_2	$k_{p2,C1}$	$k_{p2,C2}$	$k_{p2,C3}$	$k_{p2,Cj}$	r_{p2}
p_3	$k_{p3,C1}$	$k_{p3,C2}$	$k_{p3,C3}$	$k_{p3,Cj}$	r_{p3}
p_i	$k_{pi,C1}$	$k_{pi,C2}$	$k_{pi,C3}$	$k_{pi,Cj}$	r_{pi}

$\boldsymbol{R_{Cj}} = \sum \mathbf{k_{pi,Cj}} \cdot \mathbf{r_{pi}}$.

The mass balance of the chemical compounds in the batch reactor allow obtaining their variation rates as a set of equations that describes all the dynamic chemical reactions and the interactions between the components of the system (Eq. (1)).

$$\frac{dC_j}{dt} = R_{Cj} = \sum k_{pi,Cj} \cdot r_{pi} \quad (1)$$

R_{Cj} is the total variation rate for component C_j; $k_{pi,cj}$ is the stoichiometric coefficient for component C_j respect to reaction p_i; and r_{pi} is the equation rate for the reaction p_i (McCann and Meder, 2009). The R_{Cj} for each component can be easily determined from the stoichiometry matrix (Table 1) that consider the net of all reactions (Pogliani and Terenzi, 1992; Karnaukhov et al., 2007). This matrix has as columns as number of components (reagents, products) and as rows as number of reactions. Likewise, an additional column at right-hand side in the table indicates the kinetic rate equation of each reaction, which can be specified as power law expressions, etc.

This matrix is an approach for balancing chemical equations using a matrix algebra (Alberty, 1991; Gabriel and Onwuka, 2015) and follows the mass conservation principle for each reaction (rows). The variation rate of each component can be estimated by summing the columns, obtaining the aforementioned Eq. (1).

KBR generates a set of ordinary differential equations (ODE) based on the formulation of the stoichiometry matrix, which describes the evolution of each component C_j along the reaction time. After that, the resolution of the ODE system can be performed applying an appropriate implicit or explicit iterative method to achieve approximate solutions over a temporal discretized series (from the initial to the final reaction time).

3. *KBR's* graphical user interface

There are three features that should have a functional program for performing computational simulations of chemical reaction models: i) the input of kinetic rate equations of each reaction and a list of reaction times for calculation, ii) the differential equation integration algorithm and iii) the output of the calculated results in a useable format (Manka, 1999; Tóth et al., 2012). Thus, in this section we will discuss each of these three points and how they are implemented in the *KBR* application.

Fig. 1 shows a graphic representation of all the parts of the code, differentiating those that should be defined by the user (INPUT) and those generated by the software (OUTPUT).

In summary, *KBR* application allows:

1 **Formulation of kinetic models**. Definition of components (reagents, products and by products), parameters (kinetic constants, semi-saturation constants, adsorption constant, etc.),

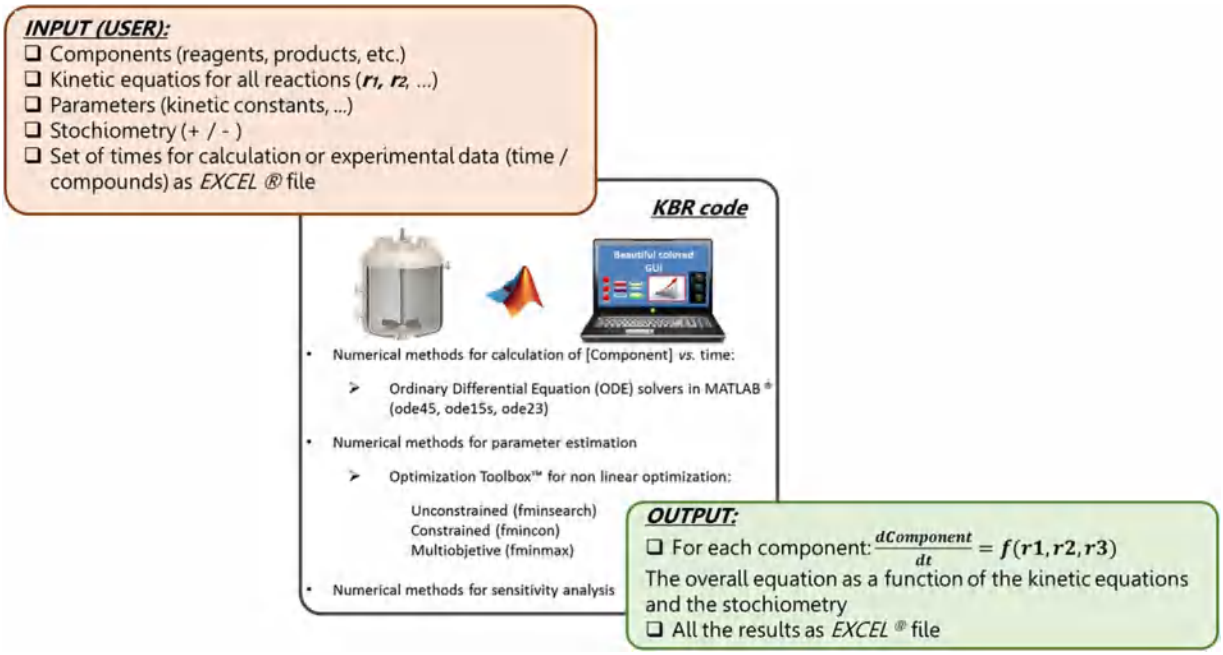

Fig. 1. Schematic description of the *KBR* application for simulation of chemical reactions in batch reactors.

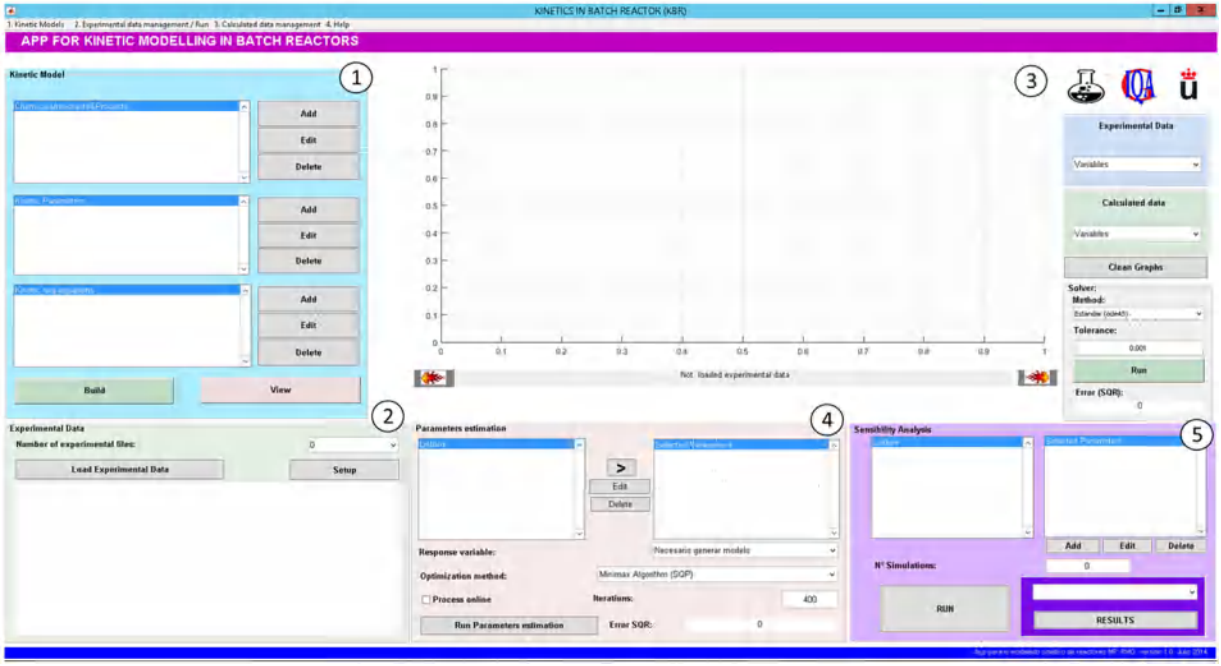

Fig. 2. Main screen of the *KBR*-GUI: 1. Kinetic model panel; 2. Experimental data panel; 3. Calculation and graphic handling section; 4. Parameters estimation panel and 5. Sensitivity analysis panel.

stoichiometry of reactions and equations (potential equations, Langmuir-Hinselwood, etc., all of them defined by the user).

2 **Model simulation**. Simulation and study of the model along the reaction time as the kinetic parameters and stoichiometry are varied.

3 **Model's parameter estimation**. The parameter estimation by uploading experimental data as Excel files.

4 **Sensitivity Analysis**. Linear sensitivity functions of key variables respect to parameters included in the analysis, determining its uncertainty according to the linear error propagation assumption.

5 **Output of the calculated data**. The model and all the results can be easily export for further analysis as Excel files.

Fig. 2 shows the main screen of *KBR's* GUI. It contains five panels: kinetic model, experimental data, calculation and graphic handling, parameters estimation and sensitivity analysis.

3.1. The kinetic model panel

This panel contains three boxes for the definition of the components, kinetic parameters and kinetic reaction rates of the model.

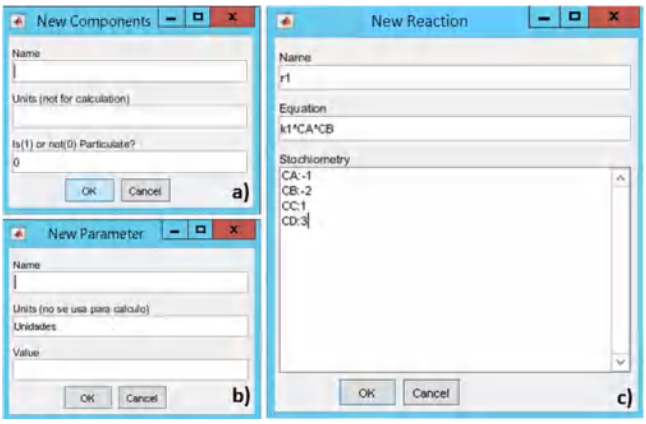

Fig. 3. Dialog box for adding a) new component, b) new parameter and c) new reaction.

The *Add* button allows the definition of new components and/or parameters (Fig. 3a and b). For components, definition of name, units (for information only) and state of the chemical, particularly if solid catalysts or solid biomass (for information only) is required. It is noteworthy that all the components and parameters should be introduced in the same unit system, since the application cannot perform automatic conversions. The parameters' box shows the kinetic parameters, stoichiometric coefficients and all the variables that are not included in componentbox. All these variables will be used in the estimation or the statistical analysis panels.

The *Add* button also allows defining the reactions of the model, including the kinetic rate equation and the stoichiometry of the reaction for each component. Fig. 3c shows an example for a simple reaction ($A + 2B \rightarrow C + 3D$) of a first order for each reactant.

Once the kinetic model is completed, the *Build* button let assembling the model properly. In this step, each component should be associated at least with one reaction equation, otherwise, an error message will appear. Components and parameters can be edited at any time. However, if new components or parameters are added to the model, or new reactions are included or edited, it is needed to build the model again, in order to update all the changes. Finally, the *View* button allows visualizing the ODE system generated by the software. The kinetic model can be saved using the option in the toolbar: Toolbar\Kinetic Models\Save.

3.2. Experimental data panel

The *KBR* simulator is able to show the concentration of all included species from initial (t_0) to final (t_f) reaction times, using the built kinetic model. It also estimates the kinetic parameters by minimizing the error between the simulated and the experimental values given for one or different experiments (replicates, experiments with different initial conditions, etc.), that can be up to 20. Each experiment data will be given as Excel file in which the first spreadsheet will be used to put in the first column the reaction times and amount of the different chemical species of the system (concentration, mass, etc.) in the following columns. The *Setup* button (see Fig. 2) permits to relate the experimental data with the components previously defined. After loading the files with the *Load experimental data* button, the *KBR* simulator enable to show the profiles of the experimental data on the right-up graph of the screen.

3.3. Solver methods and graphic handling section

The *Solver method* menu (Fig. 2) shows a selection of different Runge–Kutta methods for the calculation of the evolution of the components along the reaction time. There are three methods for solution of ODEs based on native Matlab's functions:

- **ode45**: A medium order method for non-stiff differential equations based on an explicit Runge-Kutta (4,5) formula (Dormand and Prince, 1980).
- **ode23**: An implementation of an explicit Runge-Kutta (2,3) that could be more efficient than ode45 in the presence of moderate stiffness (Bogacki and Shampine, 1989).
- **ode15s**: A variable step and variable order method for stiff differential equations, based on the numerical differentiation formulas (NDFs) of orders 1–5 (Shampine and Reichelt, 1997).

Afterwards, the tolerance for the ODE method can be selected (0.001 by default). Finally, the *Run* button calculates the results after definition of initial values for the components. The profiles of the components considering all the reactions, real experimental data and simulated by the kinetic model, will be displayed in the graph screen, being able to compare the *Experimental data* with the *Calculated data*. As example, profiles of five components (A, B, C, D and E) that are involved in three reactions (r1, r2 and r3) are shown in the screen capture of *KBR* simulator (Fig. 4). Experimental results of A and C are shown (dot points), whereas the profiles of all five components can be represented by the resolution of the kinetic model.

3.4. Parameter estimation and sensitivity analysis panels

All the parameters defined in the kinetic model will be automatically available for parameter estimation, following different methodologies from the Matlab's Optimization Toolbox:

- Function ***fminimax***: This function uses the formulation of a nonlinear programming problem that minimizes the sum of quadratic residuals (SQR) between the experimental data and those calculated by the model following a sequential quadratic programming method (Brayton et al., 1979). The maximum and minimum value of each parameter can be defined, as well as the maximum number of iterations to obtain the results.
- Function ***fminsearch***. This function uses the Nelder-Mead simplex algorithm as derivative method to solve the unconstrained minimization of the SQR between the experimental data and those calculated by the kinetic model (Lagarias et al., 1998).
- Function ***fmincon***. This function uses the interior point algorithm (Byrd et al., 2000) to find de minimum of the SQR between the experimental data and those calculated by the kinetic model.

The new optimized values of the parameters will be automatically updated in the *Kinetic model* panel.

The sensitivity analysis can be used to estimate linear sensitivity functions between estimated kinetic parameters and the calculated variables. It allows determining the uncertainty of the parameter values according to the linear error propagation assumption (Saltelli et al., 2004). *KBR* application uses the Standardized Regression Coefficients (SRC), a global sensitivity analysis method, consisting in a multivariate linear regression between the model outputs (components concentration vs. time) and a distribution of values for one parameter of the model. This method considers linear regression models, correlating the values of the parameter in a selected range (par_i) with the model outputs for those values (y_j). The sensitivity coefficient (βi) can be evaluated according to Eq. (2), where σ_{pi} and σ_y are the standard deviations

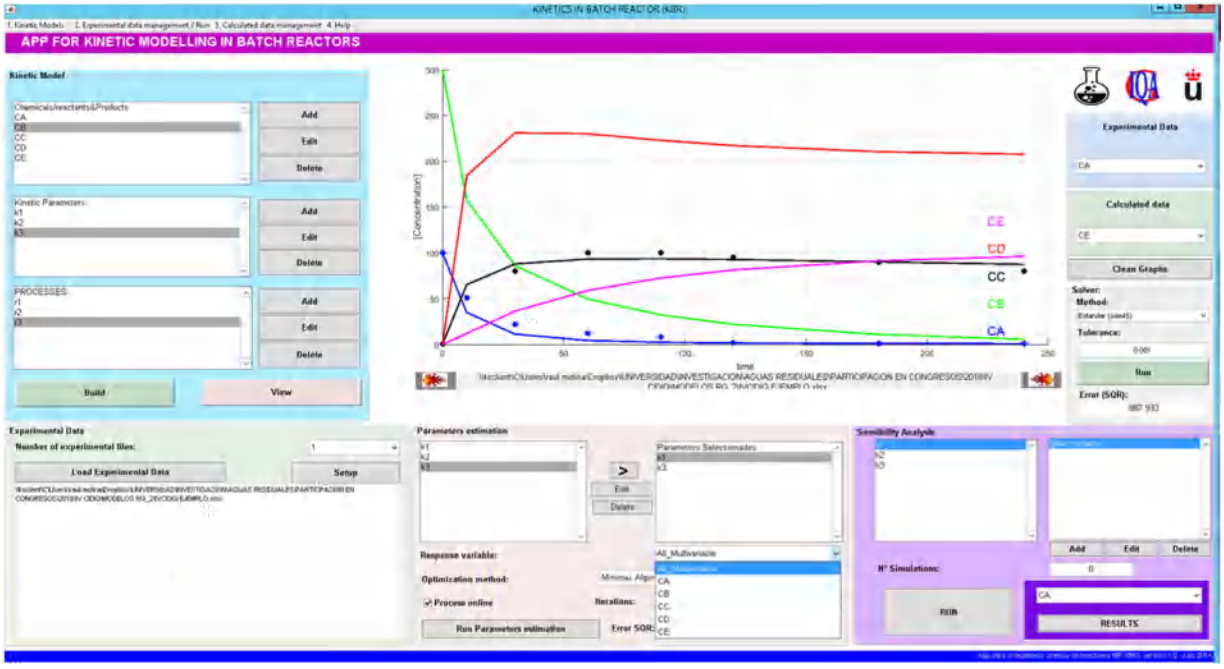

Fig. 4. *KBR* after simulation of a kinetic model of five components (A, B, C, D and E) and three reactions (r1, r2 and r3). Available experimental data: CA and CC (dot points). Simulated calculated data by the kinetic model: CA, CB, CC, CD, CE. Calculation method: ode45.

of the values given for par_i and y_j, being b_i the regression slope that correlates them (Saltelli et al., 2004; Mannina et al., 2012).

$$SRC\left(y_j, par_i\right) = \beta_i = b_i \frac{\sigma_{par_i}}{\sigma_y} \quad (2)$$

The β_i value represents a measure of sensitivity for the parameter in case that the linear regression coefficient R^2 is greater than 0.7.

4. Impact of *KBR* in final degree projects of chemical and Enviromental Engineering

The final degree project (FDP) is a subject of the fourth course of all engineering Bachelor's Degree programs at Rey Juan Carlos University. Students invest 360 h (12 ECTS, 30 h each one) and they finally elaborate a written report with the final results and defense their project by oral presentation to a well-qualified examining board. The FDP represents the culmination of the degree learning process, where students demonstrate, implement and reflect the competences acquired in different disciplines for the resolution of a given problem working autonomously under the supervision of an academic tutor.

The FDP in the Chemical Engineering and Environmental Engineering Degrees are focused in solving an industrial technical problem in which students have to develop an industrial design of a specific process, including the proposal of a technical solution, the design of auxiliary devices, control and instrumentation, location in plant, economic assessment, etc. FDPs could also address a specific scientific-technical issue in both fields -Chemical and Environmental- in which students should provide a deep discussion of their results. Herein, the *KBR* has been applied as modelling and simulation tool in FDPs for chemical reaction engineering as one of the disciplines that students aims at studying and optimizing in order to define the best reactor design in many of their FDP.

It must be pointed out that a first version of *KBR* application (*KBR_***v1**) allowed the simulation of processes in batch reactors. However, the GUI was not included and it worked as a simple Matlab script. The second version (*KBR_***v2**) included the GUI and it is current work. Based on this code for the formulation of kinetic models, estimation of parameter and sensitivity analysis, the mass balances were modified to perform the modelling and simulation of not only batch reactors but also pseudo-homogeneous continuous catalytic fixed bed reactors (*KFBR*), sequencing batch reactors (*KSBR*) and rotating biological contactors (*KRBC*) as biological processes (Molina et al., 2014), and continuous stirred tank reactors (*KCSTR*) as anaerobic digesters.

These simulator tools for the modelling of both chemical and biological reactions was used in 9 FDPs at Rey Juan Carlos University, 7 of them in Chemical Engineering and 2 in Environmental Engineering, for the three academic courses 2014/15, 2015/16 and 2016/17. The details of these FDPs are summarized in Table 2.

Fig. 5 shows the number of students with final remarks by different ranges for all the FDPs defended in Chemical and Environmental Engineering Degrees at the academic courses of 2014/15, 2015/16 and 2016/17. Results of FDPs that use the simulator tool for modelling of chemical and biological reactions are also indicated. The 9 FDPs were graded with final remarks equal or higher than 7.0 over 10 points. Particularly, 6 of them in the medium-high range of 7.0 - 7.9. The other 3 FDPs obtained a grade in the maximum range of 9–10, which is quite remarkable as only 17% of the defensed FDPs during the three academic courses in both Engineering Degrees obtained final remarks above 9.

Beside evaluation of final remarks of the DFPs, the pedagogical effectiveness of the simulator tool for modelling complex kinetic systems was also attained by the discussion between the students and tutors as described by Hernández et al. (2014). Other activities, such as surveys or questionnaires (Golman, 2016; Ospino et al., 2017), were not considered since few students used the simulator tool during each academic year. Additionally, there are significant differences between versions of *KBR_v1* and *KBR_v2* and *KFBR*, *KSBR*, *KRBC* and *KCSTR* (focused on different operation modes) that make difficult the comparison through these methodologies. Nevertheless, the supervisors observed that students were able to afford more complex approaches to chemical or biological reaction networks, taking advantage of the simplicity of *the* simulator tool for modelling and parameter estimation, instead of programming the

Table 2
List of Final Degree Projects that use the simulation tool of Kinetics in different reactors (*KBR, KSBR, KRBC, KFBR and KCSTR*).

Title	*Kinetic simulation verison*[1]	Degree[2]	Final mark (0-10.0)	Overall results: Number of students (CE + EE)[2] earned the following grades					
				<5.0	5.0-5.9	6.0-6.9	7.0-7.9	8.0-8.9	9.0-10.0
Academic Course: 2014/15 (41 students evaluated)									
Modelling the treatment of phenolic aqueous solutions by a heterogeneous Fenton-like process in a batch reactor.	*KBR_v1*	CE	7.4	5(12%)	1(2%)	5(12%)	20(50%)	2(5%)	8(19%)
Modelling the treatment of phenolic aqueous solutions by a heterogeneous Fenton-like process in a batch reactor. Effect of parallel-side reactions.	*KBR_v2*	CE	7.0						
Modelling the production of diaryl-ethers using a heterogeneous catalyst (Cu-MOF-74).	*KBR_v2*	CE	7.5						
Modelling a RBC unit for urban wastewater treatment.	*KRBC*	CE	7.0						
Design of a sequential batch reactor for industrial wastewater treatment.	*KSBR*	EE	9.3						
Modelling a RBC unit for urban wastewater treatment.	*KRBC*	EE	9.3						
Academic Course: 2015/16 (48 students evaluated)									
Design of a RBC unit for the treatment of urban wastewater streams with removal of emerging pollutants.	*KRBC*	CE	7.8	2(4%)	9(19%)	13(27%)	11(23%)	6(12%)	7(15%)
Academic Course: 2016/17 (50 students evaluated)									
Design and modelling of a FBR for the treatment of phenolic aqueous solutions by heterogeneous Fenton-like reactions.	*KFBR*	CE	7.3	2(4%)	9(18%)	7(14%)	18(36%)	6(12%)	8(16%)
Design of an anaerobic digester simulator with implementation of ADM1 model and further modifications.	*KCSTR*	CE	8.0						
TOTAL for the three Academic Courses				9(6%)	19(14%)	25(18%)	49(35%)	14(10%)	23 (17%)

[1]Version of simulation tool for reactions in: batch mode *(KBR_v1 and KBR_v2*; without and with GUI, respectively), continuous operation mode in catalytic fixed bed reactor(*KFBR*) and semi-continuous and continuous operation mode in sequencing batch reactors (*KSBR*), rotating biological contactors *(KRCB*) and continuous stirred tank reactor (*KCSTR*) as different biological reactors.
[2]Degree: CE (Chemical Engineering), EE (Environmental Engineering).
[3]Include both students of CE (Chemical Engineering) and EE (Environmental Engineering).

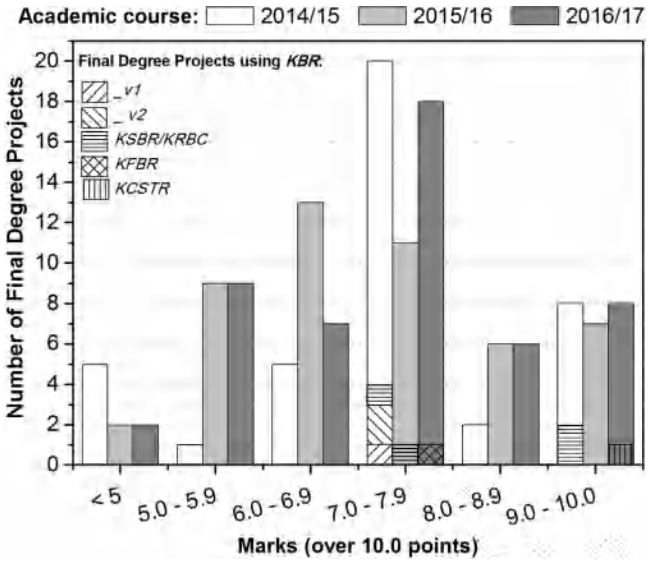

Fig. 5. Distribution of marks of FDPs defensed in the last three academics courses including those carried out using the simulation tool for modelling al simulation of chemical and biological reactions.

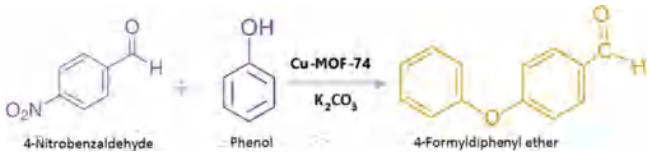

Fig. 6. Scheme of the cross-coupling C–O reaction of phenol with nitroarenes.

solution in Matlab. This allowed a better understanding of the processes simulated with the program, a more accurate discussion of the results and consequently more precise conclusions.

Concerning the three FDPs performed using the *KBR_v1* and *KBR_v2* for modelling and simulation of chemical reactions in batch reactors (Table 3), the comparison of cases 1 and 2 reveals that the student using *KBR_v2* could replicate the work performed by the student programming in Matlab (*KBR_v1*), but adding more parallel reactions to the process. Consequently, the second student proposed a more accurate description of the overall process. In case 3, the student proposed a more complex reaction mechanism for a different application, that included reversible reactions, adsorption and desorption of reactants and products, as well as evaluation of activation energy for the reactions involved in the model. Actually, the use of *KBR* helped the student to acquire a deep understanding of the physico-chemical processes occurring in that catalytic system. This case will be shown and explained in the following section.

5. Example of Kinetics in Batch Reactor (*KBR*) application for modelling of cross-coupling C-O reaction

This example shows a brief review of the application of *KBR* in a Final Degree Project in Chemical Engineering entitled "Modelling the production of diaryl-ethers using a heterogeneous catalyst (Cu-MOF-74)". The main objective of this FDP was modelling a catalytic system for the production of diaryl-ethers through a cross-coupling reaction of phenol and 4-nitrobenzaldehyde (Fig. 6), using the experimental results obtained by a metal-organic framework material as heterogeneous catalyst.

Table 3
Cases of FDPs performed with KBR for modelling and simulation of chemical reactions in batch reactors.

CASE	Title	*KBR* Version	Particular details of the project
1	Modelling the treatment of phenolic aqueous solutions by a heterogeneous Fenton-like process in batch reactor.	*KBR_v1* (Matlab code without GUI)	Lumped kinetic model with two reactions. Parallel reactions Parameter estimation: kinetic constants.
2	Modelling the treatment of phenolic aqueous solutions by a heterogeneous Fenton-like process in a batch reactor. Effect of parallel-side reactions.	*KBR_v2* *(KBR* described in this paper*)*	Lumped kinetic model with two reactions. Parallel reactions. Leaching of active phase from the heterogeneous catalyst. Contribution of homogeneous catalysis to the overall performance. Parameter estimation: kinetic constants.
3	Modelling the production of diaryl-ethers using a heterogeneous catalyst (Cu-MOF-74).	*KBR_v2 (KBR* described in this paper*)*	Kinetic model with two reactions Reversible reactions Sorption and desorption of reagents and products Influence of the catalyst loading to the kinetics Parameter estimation: kinetic constants, activation energy and pre-exponential factor according to Arrhenius equation.

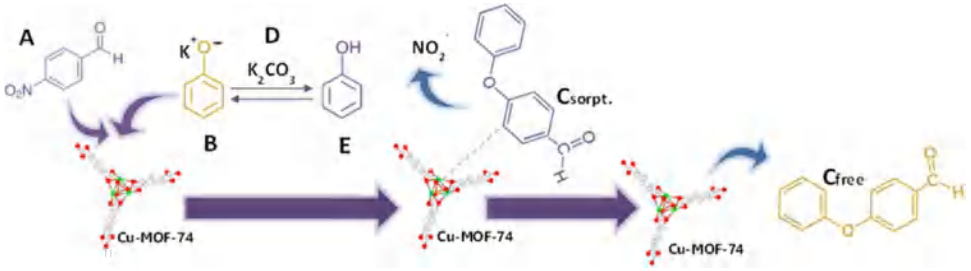

Fig. 7. Proposed reaction mechanism for the cross-coupling C—O reaction using Cu.MOF-74 as heterogeneous catalyst.

Table 4
Reactions and physical processes with the corresponding kinetic equations of the proposed mechanism for the production of 4-formyldiphenyl ether using a heterogeneous catalyst through the cross-coupling of phenol and 4-nitrobenzaldehyde.

Reaction / process		Kinetic rate equation	
$A + B \rightarrow C^*$	(Reaction R6)	$r_1 = k_1 C_A C_B$	(3)
$C^* \rightarrow C + catalyst$	(Reaction R5)	$r_2 = k_2 C_{C^*}$	(4)
$E \leftrightarrow B$	(Reaction R2)	$r_3 = k_3 C_E$	(5)
		$r_4 = k_4 C_B$	(6)
$\frac{dC_A}{dt} = -k_1 C_A C_B$	(7)		
$\frac{dC_B}{dt} = k_3 C_E - k_1 C_A C_B - k_4 C_B$	(8)		
$\frac{dC_{C^*}}{dt} = k_1 C_A C_B - k_2 C_{C^*}$	(9)		
$\frac{dC_C}{dt} = k_2 C_{C^*}$	(10)		
$\frac{dC_E}{dt} = -k_3 C_E + k_4 C_B$	(11)		
$\frac{dC_F}{dt} = \frac{dC_B}{dt} + \frac{dC_E}{dt}$	(12)		

The supervisor provided to the student experimental results of reactions performed at different phenol/4-nitrobenzaldehyde molar ratios, catalyst loadings and temperatures (Leo et al., 2017). At the end of the project, the student developed and simulated a reaction mechanism based on the adsorption/desorption of reagents and products over the surface of the porous solid Cu-MOF-74 catalyst and the chemical reaction. Additionally, the student calculated the Arrhenius parameters of the kinetic reaction constants, pre-exponential factor (*ln A*) and activation energy (*Ea*) for the cross-coupling C–O reaction.

The final mechanism used for the modeling of the process is depicted in Fig. 7, where the chemical components involved in the mechanism are as follows:

- **A**: 4-nitrobenzaldehyde (reagent).
- **B**: Phenolate (reagent).
- **C**: 4-Formyldiphenyl ether (product).
- **D**: Potassium carbonate (base in excess, K_2CO_3).
- **E**: Phenol (reagent).
- **F = B + E** (sum of phenol and phenolate form)

Several assumptions were made to establish the reactions involved in the model:

- Active copper sites are identical and homogeneously distributed on the catalyst surface.
- The reagents A (4-nitrobenzaldehyde), B (phenol in its phenolate form) can be adsorbed (A^* and B^*) in any of the active copper sites available on the catalyst surface.
- The product C (4-formyldiphenyl ether) can be formed and retained over any of the active copper sites on the catalyst surface (C^*) before being desorbed.
- Partial first order to reactants for all the elementary steps is assumed.

Thus, the reactions and physical processes that were described according to proposed reaction mechanism and assumptions are summarized from reaction R1 to R5.

$$A + Catalyst \rightarrow A^* \quad (R1)$$

$$E \leftrightarrow B \quad (R2)$$

$$B + Catalyst \rightarrow B^* \quad (R3)$$

$$A^* + B^* \rightarrow C^* \quad (R4)$$

$$C^* \rightarrow C + Catalyst \quad (R5)$$

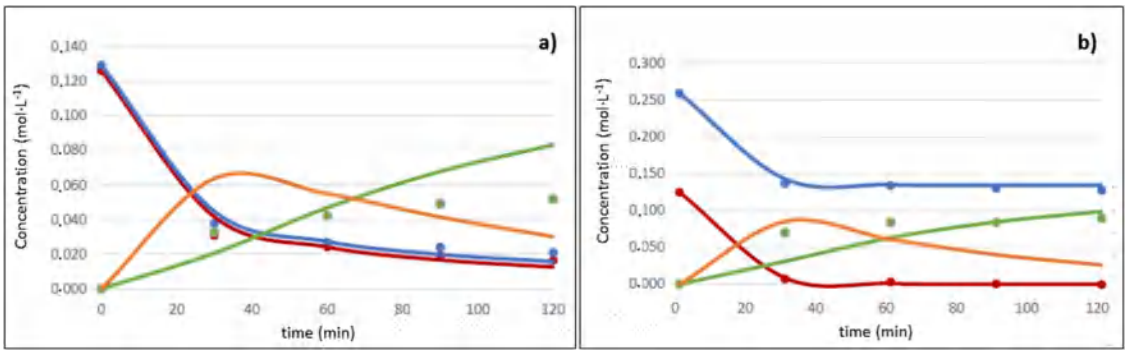

Fig. 8. Experimental (dots) and calculated (lines) values of C_A ( ), C_F ( ), C ( ) and C^* ( ) for reactions at 120 °C, 5% wt. of catalyst and initial (F/A) molar ratio of a) 1 and b) 2.

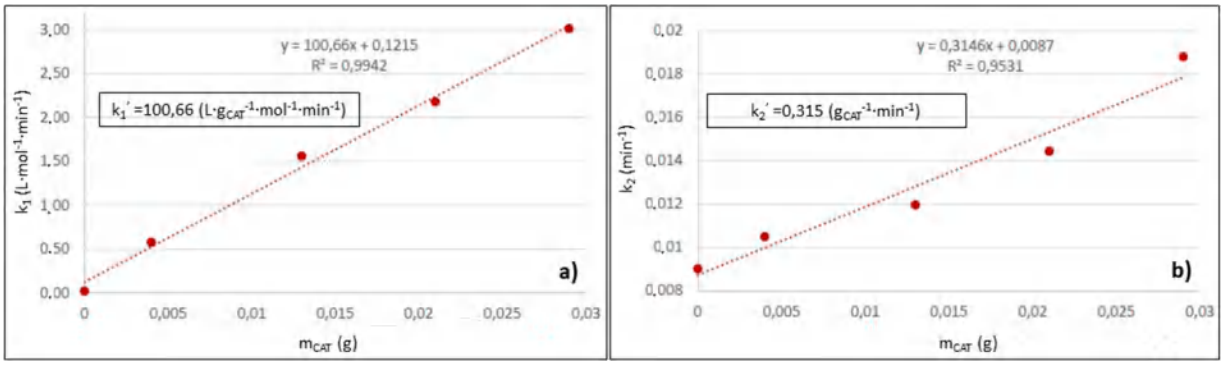

Fig. 9. Influence of the catalyst concentration in apparent constants k_1 and k_2 and calculation of intrinsic constant k_1' and k_2' at 120 °C.

According to previous studies, it could be proven that A and B (as 4-nitrobenzaldehyde and phenolate form of phenol) are quickly adsorbed over catalyst surface and are not limiting the chemical reaction rate. By this reason, the physical adsorption process of A and B were discarded of the model, enabling that reactions 1 and 3 could be simplified in only the reaction R6.

$$A + B \rightarrow C^* \quad \text{(R6)}$$

On the other hand, the desorption process of the C^* product (4-formyldiphenyl ether) from the catalyst surface was not ruled out of the model in order to assess if this physical process can affect the overall rate of chemical transformation.

Once all the reactions and physical processes of the mechanism are set out, the kinetic equations for the chemical reactions as well as the desorption process of the product (4-Formyldiphenyl ether, C) are defined as displayed in Table 4.

According to the previous sections, the model can be formulated in the Kinetics in Batch Reactor (*KBR*) application following these steps:

- Definition of components: A, B, C, C^*, E and F as B + E.
- Definition of kinetics and stoichiometry of each reactions or physical process: Reactions 2, 5 and 6; Kinetic rate Eqs. (3)–(5) and 6 (see Table 4)
- Definition of kinetic parameters of kinetic rate equations (k_1–k_4).

In a first approach, the parameters were estimated using experimental data (A, F as sum of phenol and phenolate form and C) measured in the catalytic experiments performed with a fixed catalyst concentration and temperature, but different initial concentrations of A and F. Fig. 8 shows the results obtained for F/A molar ratios of 1 and 2, whereas the values of k_1 – k_4 are depicted in Table 5.

Table 5
Values of kinetic constants calculated for experiments at 120 °C, 5% wt. of catalyst and initial (F/A) molar ratio of 1 and 2.

Parameter	Value
k_1 ($L \cdot mol^{-1} \cdot min^{-1}$)	2.180
k_2 (min^{-1})	0.014
k_3 (min^{-1})	0.853
k_4 (min^{-1})	2.643

Table 6
Parameters of the Arrhenius equation for k_1'.

	Ln A	A	-Ea/R (K)	Ea ($J \cdot mol^{-1}$)
k'$_1$ ($L \cdot mol^{-1}$ min^{-1})	5,37	**214**	−318	**2648**

Taking into account results of experimental reaction performed at different catalyst loadings (Leo et al., 2017), the student was also able to evaluate the influence of the catalyst concentration in apparent constants k_1 and k_2 was also assessed (Fig. 9). It allows obtaining the kinetic constants independent of the catalyst concentration for equations A + B → C^* (k_1') and C^* → C + Catalyst (k_2').

The student was also able to determine the Arrhenius kinetic parameters of chemical reaction constants such as the case of reaction of chemical A + B → C^* by the representation of the apparent kinetic (k_1') at different temperatures and fitting the results to Arrhenius equation. Table 6 shows the values of the Arrhenius kinetic parameters for the kinetic contant k_1'. The profiles of reactants (A and F) and product (C) for the different temperatures are depicted in Fig. 10.

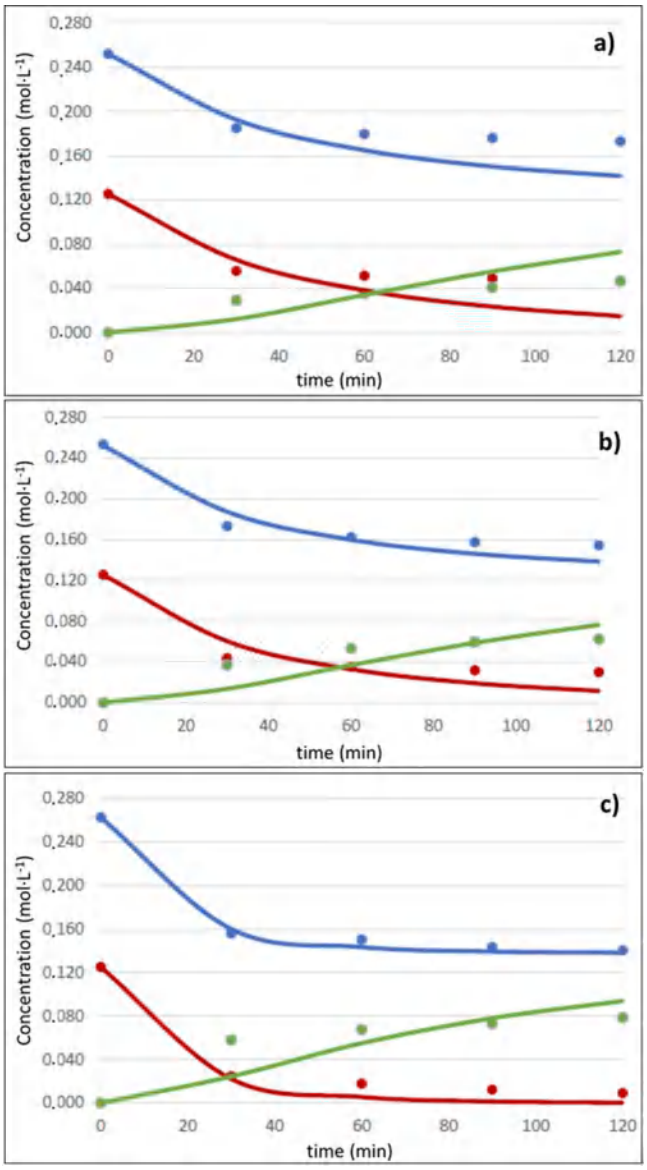

Fig. 10. Experimental (dots) and calculated (lines) values of C_A ( ), C_F ( ) and C ( ) for reactions at with 5% wt. of catalyst, (F/A) molar ratio of 2 at different temperatures: a) 60 °C, b) 80 °C and c) 100 °C.

From this FDP, some interesting conclusions about this chemical transformation system were extracted:

1) The chemical rate conversion of phenol (B) and 4-nitrobenzaldehyde (A) to 4-formyldiphenyl ether (C) is controlled by the rate of the deprotonation of phenol (B) to phenolate (F) in the basic media, as the equilibrium constant of reaction E ↔ B is lower than he kinetic constant of the principal reaction A + B → C*.
2) The excess of phenol led to the increase of the yield to 4-formyldiphenyl ether (C) with maximum concentrations of the product in short reaction times.
3) The physical adsorption/desorption of the C product over the catalyst surface seems to be a critical factor that is affecting the final concentration of C in the liquid phase of the reaction medium.
4) The Arrhenius kinetic parameters of chemical reactions were determined by the study of reaction experiments at different temperatures for the heterogeneous catalyst and the effect of this variable on the overall performance for the cross-coupling C-O reaction was observed.

6. Conclusions

The KBR application allows the evaluation of the kinetics of simple and complex chemical batch processes through a friendly graphical user interface. This application is proposed as a valuable tool to model multiple reaction mechanisms and study the influence of critical variables in these systems. The program provides an easy method to define mechanistic reaction pathways and user-made kinetic equations for subsequent parameter estimation and sensitivity analysis. This simulator application is considered a very interesting tool to understand the kinetics of chemical reactions in batch reactors, not only for FDP purposes, but also for research on chemical reactions modelling. This can be also a very useful in scale-up of batch reactors without the need of further experimental studies. The application of this simulator tool in FDP for Chemical and Environmental Engineering degrees have evidenced that students are able to accomplish more complex mechanistic systems, taking advantage of the simplicity of the simulator tool for modelling and parameter estimation, as the case of the example reported in this work for modelling a cross coupling C–O reaction using a heterogeneous catalyst (Cu-MOF-74) for the production of diaryl-ethers.

7. Software Availability

The *KBR* files and a quick start guide are supplied as supporting information into a zip file. You should take into account that KBR runs under the MATLAB® software environment. Support for application and implementation of processes in *KBR* will be willingly provided upon request. To express interest, please contact Dr. Raul Molina (raul.molina@urjc.es), Dr. Gisela Orcajo (gisela.orcajo@urjc.es) or Dr. Fernando Martínez (fernando.castillejo@urjc.es) at Rey Juan Carlos University (Spain).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ece.2018.11.003.

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