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## Parameter estimation with estimability analysis applied to an industrial scale polymerization process

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### ABSTRACT

This paper aims to estimate the parameters of a complex model representing an industrial scale polymerization process. The estimability analysis of the parameters prior to estimation allows simplifying the optimization problem but it is usually neglected in literature when industrial data is used for estimation. In this case, though, the estimability analysis would be even more important since usually less data is available, they are associated with a higher uncertainty and the experiments might not be designed as in laboratory or pilot plant. The orthogonalization method reduced from 68 to 29 the number of parameters of the model. Polymer properties, which are measured offline with low frequency, as well as process temperatures and flow rates are used for validating the model. Small deviations, up to 5%, between model prediction and experimental data indicate the quality of fit of the model and the importance of carrying out first an estimability analysis.

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### 1. Introduction

The mathematical modeling must describe the process in an accurate and generalized manner, providing a trustworthy mechanism for evaluating the studied phenomena. In order to obtain accurate and reliable phenomenological model, the parameter estimation is a critical step, since incorrect parameters might lead to a significant degradation of the model predictive capacity (Benyahia et al., 2013).

When approaching polymerization processes modeling, the parameters estimation becomes even more important and challenging due to the complex and large-scale models. These models present a great number of unknown parameters, which describes, a.o., quality properties such as melt index and density, kinetic constants, physical and transport properties, such as heat capacity and viscosity. In order to estimate these parameters, experimental data must be available, either from laboratory or industrial scale.

Although modeling and parameter estimation for polymerization reactors have been vastly studied in the last decades (Charpentier et al., 1997; Kou et al., 2005; Kiparissides 2006; Embiruçu et al., 2008; Mogilicharla et al., 2014; Pater et al., 2002), just a few number of works performs an estimability analysis in order to evaluate which parameters should indeed be estimated

and very few works focus on industrial scale models, considering the challenges faced in this case (Mjalli and Ibrehem, 2011).

Estimability tries to indicate the parameters with higher impact on the model output, classifying them in order of influence. According to Quaiser and Mönnigmann (2009), the methods of estimability analysis try to verify the viability of estimating the parameters of a model based on the input and output data of the system. This preliminary step is particularly critical in the parameter estimation of complex models, as the ones for polymerization processes, as they normally present dozens of parameters which might be correlated. In these cases, it may be impossible to estimate the whole set of parameters due to their correlations and the limited amount of data available. The preliminary analysis of estimability, thus, allows simplifying the optimization problem due to the lower number of parameters to estimate.

The objective of this work is to estimate the parameters of a phenomenological model representing an industrial scale polymerization reactor (Pontes et al., 2010), carrying out first an estimability analysis. The high pressure and temperature conditions hinder a precise representation of the system by pilot plant or laboratory experiments, practices which are very costly. The alternative then is to use measurements directly obtained at the industrial practice. This approach usually offers some challenges since experiments cannot be designed for this purpose and lower amount of data is available because not every variable, like the polymer properties, can be measured online. A preliminary analysis becomes then even more important to reduce the number of parameters to be

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estimated since some of them might be correlated or might not influence process outputs.

Table 1 presents a group of published works in the last decade about parameters estimation applied to polymerization processes. It indicates the studies which perform a preliminary analysis of the parameters as well as the scale where the data were collected. The works which perform the estimability analysis use laboratorial or pilot plant data. Yao et al. (2003), when estimating the parameters of the ethylene gas phase copolymerization with Ziegler-Natta catalyst, developed the orthogonalization method. Benyahia et al. (2013) use the orthogonalization method (Yao et al., 2003) when approaching the copolymerization of styrene with butyl acrylate at lab scale. Due to the high number of parameters to estimate (49), the authors reports difficulties predicting some polymer properties: mass fraction, average weight and numerical molecular weights and average particles' diameter. The orthogonalization reduced the number of parameters to be estimated to 21, allowing a successful estimation of the parameters. Kou et al. (2005) present a well-constructed study about the preliminary analysis of parameters when approaching the phenomenological model of the copolymerization of ethylene with 1-butene in a gas phase pilot reactor with metallocene catalysts. The model validation focuses on polymer properties, such as the incorporated molar fraction of comonomer, the average weight and numerical molecular weights, all of which measured experimentally. The authors use the estimability based on orthogonalization to reduce the number of parameters to be estimated from 22 to 17, thus allowing the satisfactory validation of the model.

Although the extensive bibliographical review, any work approaching industrial scale process was found to carry out the estimability analysis. Hvala et al. (2011) present a mathematical model with 44 parameters for the vinyl acetate emulsion polymerization. The model was validated through trial and error adjustment of the parameters. Embiruçu et al. (2000) develop the phenomenological model for the homopolymerization of ethylene in solution with Ziegler-Natta catalyst in a series of tubular and stirred tank reactors. The model comprehends 28 parameters, which were satisfactorily estimated using plant data by Embiruçu et al. (2008). Pontes et al. (2010) extend this model to the copolymerization of ethylene with 1-butene, process investigated here. The resulting model presents 68 parameters which were estimated based on stationary synthesis conditions, due to the unavailability at that time of historical data from plant or literature. The current study, then, aims to estimate these parameters using historical data from industry. Given the high number of parameters to be estimated, even comparatively to the works presented in Table 1 and the possibility of correlation between them, the preliminary analysis of the parameters is carried out here.

The parameter estimation from industrial data presents a set of challenges and demands a thorough preliminary analysis. On the one hand, laboratory scale experiments might be planned in order to obtain the required data for estimation and are carried out at more controlled conditions. On the other hand, measurements from the industrial practice take historical data available so that the operating conditions are not planned and the data is less precise. When data is collected from laboratory or pilot plant, measurements of the polymer properties are more easily available and might be more representative of the reaction's conditions since samples might be taken at the reactor outlet with the desired frequency. In industry, however, polymer properties such as the molecular weight are not usually quantified. The practice is to measure quality variables such as melt index and density with a frequency much slower than the process time constant and with high delays.

The parameters of the quality correlations have to be estimated among the other parameters which describes kinetic rates, physical

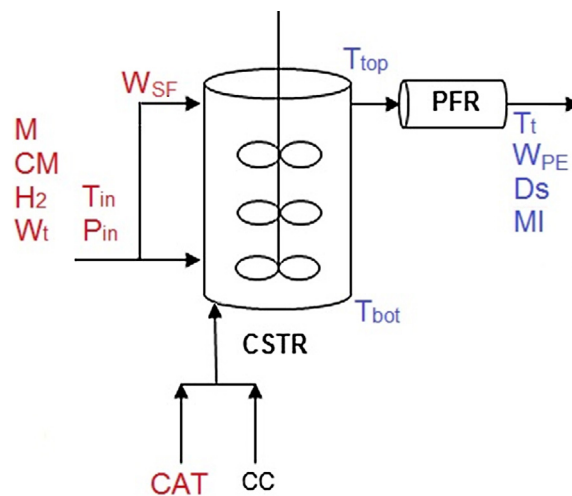


Fig. 1. Process representation.

and transport properties correlations. Despite the large number of unknown parameters, only reactor's temperature and polymer production rate are frequently measured. Estimability analysis is then the key to successful parameter estimation. The parameter estimation of a large scale phenomenological model using industrial data with previous estimability analysis is, therefore, an important contribution of this work.

The estimability analysis based on orthogonalization (Yao et al., 2003) is used. Additionally to the methodology developed by Yao et al. (2003), an analysis of the eigenvalues of the Hessian matrix is carried out in order to evaluate if a global optimum can be found. If the Hessian matrix is not positive-definite and a local optimum might be found, the estimability analysis is repeated until the parameter values do not change significantly. We show how the estimability analysis allows improving the quality of fit of the model so that it should not be ignored as the literature usually does when approaching industrial scale models.

This manuscript is organized as follow. First, the case study is described in Section 2. In Section 3 the estimability analysis based on the orthogonalization method is presented, followed by the optimization problem description in Section 4. The results and discussion are presented in Section 5 and the conclusions, in Section 6. An Appendix A illustrates the orthogonalization method step by step with a small case study.

## 2. Mathematical model

The process studied comprises a non-ideal continuous stirred tank reactor (CSTR), followed by a tubular reactor PFR (*Plug Flow Reactor*), which has the goal of completing the conversion, as illustrated by Fig. 1. This is a representation of an industrial polymerization reactor located in the Camaçari Petrochemical Pole—Brazil. The input variables include concentration of ethylene (monomer, M), concentration of butene (comonomer, CM), concentration of hydrogen (chain transfer agent, H<sub>2</sub>), concentration of catalyst (CAT), concentration of co-catalyst (CC), total flow rate (W<sub>t</sub>) and side feed (W<sub>SF</sub>), which feeds the top of the CSTR and helps the mixing inside the reactor. The output variables used to estimate and validate the model are the CSTR top and bottom temperatures, T<sub>top</sub> and T<sub>bot</sub>, respectively, the PFR outlet temperature, T<sub>t</sub>, the polymer production rate, W<sub>PE</sub>, the melt index, MI, and the polymer density, Ds. Unlike temperatures and polymer production, the polymer properties are not measured online.

**Table 1**  
Studies approaching parameter estimation of polymerization reactors.

Authors and year	Reaction Mechanism	Monomer	Number of Parameters	Estimability Analysis	Plant Type	Parameter Type
Mogilicharla et al. (2014)	SL	H	12	N	L	K
Benyahia et al. (2013)	E	C	49	Y	L	K/PP
Xiaojun et al. (2012)	ST	H	9	N	I	K
Mjalli and Ibrehem (2011)	G	H	9	N	I	P
Hvala et al. (2011)	E	H	44	N	I	K/PP
Lin et al. (2010)	SS	H	19	Y	L	K
Pontes et al. (2010)	SL	H	36	N	I	K/PP
Embiruçu et al. (2008)	SL	H	28	N	I	K/PP
Kou et al. (2005)	G	C	22	Y	L	K/PP
Yao et al. (2003)	G	H	50	Y	L	K/PP

C, Copolymerization; E, Emulsion; G, Gaseous phase; H, Homopolymerization; I, Industrial; K, Kinetic; L, Laboratory; N, Do not perform the estimability analysis; PP, Polymer properties; SL, Solution; SS, Suspension; ST, Slurry; Y, Perform estimability analysis.

The quality variables are correlated with the polymer molecular weight and the content of comonomer incorporated into the polymeric chain. If measurements of these properties were available, it would be straightforward to calculate the parameters of melt index and density correlations. This is, though, not the case of the polymerization process investigated here, which measures only the quality variables (melt index and density) with a sampling time higher than 60 min, while the process dynamics has order of few minutes (Pontes et al., 2015). The sample is collected at the end of the process, at the extruder, during the sampling interval, so that it is a mixture of the polymer produced within this period. Therefore, besides the transport delay, the measurement does not correspond precisely to the polymer produced at a specific time instant, as in pilot plant experiments. The measurements of the polymer properties, therefore, have an uncertainty, which might be taken into account when evaluating the results of the model validation. These are some of the challenges faced when estimating parameters using historical data from industry.

Measurements of the input and output variables indicated in Fig. 1 are collected during one month of operation with a sampling interval of one minute, covering the production of different polymer grades. Measurements of the quality variables are only available at every one or two hours, so that the last measurement is still used by operators until a new one becomes available. Due to the transport delay, MI and Ds measurements are delayed one hour, value estimated from the process residence time. The data set was analyzed in order to select the intervals which operate with 1-butene, since the same process produces homopolymer and copolymer with octene. The data set was filtered in order to remove high-frequency noise. After data reconciliation a set with around 500 experimental data points was chosen, ensuring the presence of grade transitions in order to represent the process dynamics as well as different steady states. The data set was split into two sets, one to be used for the parameter estimation and the other, for the model validation.

The kinetic model of the copolymerization reaction was described by Pontes et al. (2010) and is summarized in Table 2, where C is catalyst, CC is co-catalyst, C\* is active catalyst, I<sub>C</sub> and I<sub>CC</sub> are impurities that poison the catalyst and co-catalyst respectively, CCD is deactivated co-catalyst, CD is deactivated catalyst, H<sub>2</sub> is hydrogen, M<sub>1</sub> and M<sub>2</sub> are monomers, P is live polymer chain with terminal monomer type 1, Q is live polymer chain with terminal monomer type 2, U is dead polymer and the subscripts p and q are the number of units of monomer 1 and 2, respectively. A more comprehensive mechanism also considers termination reactions with monomer, transfer agent and organometallic as suggested by Embiruçu et al. (2000) when modeling the homopolymerization process, therefore these reactions are additionally considered here. The activation and poisoning reactions take place very quickly and are considered instantaneous so their kinetic constants do not

need to be estimated. The kinetic constants are described by the Arrhenius law:

$$k_j = A_j e^{-\frac{E_j}{RT}} \quad (1)$$

where  $E$  is the activation energy,  $A$  is the frequency factor,  $R$  is the universal gas constant,  $T$  is the temperature and the subscript  $j$  refers to the reaction presented in Table 2. Therefore, there are 54 kinetic parameters to be estimated for the 27 kinetic rates presented in Table 2.

Pontes et al. (2010) developed the first principles of dynamic modeling for the copolymerization reactor illustrated in Fig. 1. The reader should refer to the original reference for more details on the mathematical modeling. Here, only the equations which depend on the unknown parameters are presented in Table 3 for the sake of simplicity. The CSTR non-ideality is taken into account through a mixing stream ( $B$ ) between adjacent ideal CSTR zones. In Table 3,  $\theta$  is the unknown parameter,  $\overline{MW}_w$  is the polymer average weight molecular weight,  $\delta$  is the comonomer content incorporated into the polymer,  $T$  is temperature,  $\rho$  is the mixture specific mass,  $V$  is the volume of the ideal CSTR zone,  $Rot$  is the rotation of the agitator and  $W$  is the feed to the ideal CSTR zone (Pontes et al., 2010). Therefore, there are 14 unknown parameters for the correlations presented in Table 3. They have to be estimated together with the kinetic constants to validate the mathematical model so that there are 68 parameters to be estimated.

The mathematical model of the PFR is given by a system of partial differential equations which have been transformed into ordinary differential equations by the characteristics method. The reactor system is then described by a differential algebraic equations (DAE) system with 120 ordinary differential equations. The algorithm is implemented in Fortran and integrated using the LSODE code (Hindmarsh, 1980).

### 3. The estimability analysis

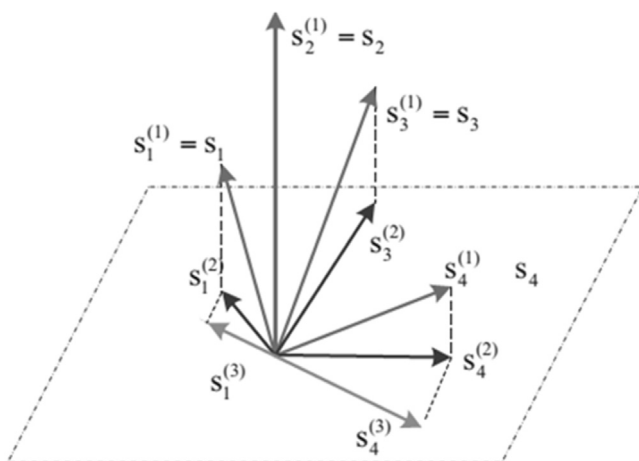
The orthogonalization method for estimability analysis was firstly proposed by Yao et al. (2003). The authors show the efficiency of the method by reducing the number of estimable parameters from 50 to 22. Fig. 2 illustrates the Gram-Schmidt principle of orthogonalization (Kravaris et al., 2013). Considering four parameters,  $S_1, S_2, S_3$  e  $S_4$ , their sensitivity vectors are represented as:  $S^{(1)}_1, S^{(1)}_2, S^{(1)}_3$  e  $S^{(1)}_4$ . The first selected parameter is the one that presents the biggest sensitivity parameter, in this case  $S^{(1)}_2$ . The sensitivity vectors of the other parameters are represented orthogonally in the perpendicular plane to the sensitivity vector of the selected parameter. The process is repeated until all the parameters are selected or until the biggest sensitivity vector is lower than a defined tolerance limit (Kravaris et al., 2013). The orthogonalization is thereby an algebraic tool that seeks to obtain a vector linearly independent from two other vectors, eliminating the linear

**Table 2**  
Kinetic model (Pontes et al., 2010).

Reaction	Rate	Reaction	Rate
Activation ( $s^{-1}$ ) $C + CC \rightarrow C^*$	$k_f \cdot [C_n] \cdot [CC]$	Transfer to hydrogen ( $m^{0.5} \text{ mol}^{-0.5} s^{-1}$ ) $P_{p,q} + H_2 \rightarrow C^* + U_i$	$k_{fh,1} \cdot [H_2]^{0.5} \cdot [P_{p,q,n}]$
Poisoning ( $s^{-1}$ ) $I_{CC} + CC \rightarrow CCD$	$k_{iCC} \cdot [I_C] \cdot [CC]$	$Q_{p,q} + H_2 \rightarrow C^* + U_i$	$k_{fh,2} \cdot [H_2]^{0.5} \cdot [Q_{p,q,n}]$
$I_{C^*} + C^* \rightarrow CD$	$k_{iC} \cdot [I_{C^*}] \cdot [C_n^*]$	Transfer to organometallic ( $m^{0.5} \text{ mol}^{-0.5} s^{-1}$ ) $P_{p,q} + CC \rightarrow C^* + U_{p,q}$	$k_{ft,1} \cdot [CC]^{0.5} \cdot [P_{p,q,n}]$
Initiation ( $m^3 \text{ mol}^{-1} s^{-1}$ ) $C^* + M_1 \rightarrow P_{1,0}$	$k_{i,1} \cdot [M_1] \cdot [C_n^*]$	$Q_{p,q} + CC \rightarrow C^* + U_{p,q}$	$k_{ft,2} \cdot [CC]^{0.5} \cdot [Q_{p,q,n}]$
$C^* + M_2 \rightarrow Q_{1,0}$	$k_{i,2} \cdot [M_2] \cdot [C_n^*]$	Spontaneous termination ( $s^{-1}$ ) $P_{p,q,n} \rightarrow CD + U_{p,q}$	$k_{t,1} \cdot [P_{p,q,n}]$
Propagation ( $m^3 \text{ mol}^{-1} s^{-1}$ ) $P_{p,q} + M_1 \rightarrow P_{p+1,q}$	$k_{p,1,1} \cdot [M_1] \cdot [P_{p,q,n}]$	$Q_{p,q,n} \rightarrow CD + U_{p,q}$	$k_{t,2} \cdot [Q_{p,q,n}]$
$P_{p,q} + M_2 \rightarrow Q_{p,q+1}$	$k_{p,1,2} \cdot [M_2] \cdot [P_{p,q,n}]$	Termination with monomer ( $m^{0.5} \text{ mol}^{-0.5} s^{-1}$ ) $P_{p,q} + M_1 \rightarrow CD + U_{p,q}$	$k_{tm,1,1} \cdot [M_1] \cdot [P_{p,q,n}]$
$Q_{p,q} + M_1 \rightarrow P_{p+1,q}$	$k_{p,2,1} \cdot [M_1] \cdot [Q_{p,q,n}]$	$P_{p,q} + M_2 \rightarrow CD + U_{p,q}$	$k_{tm,1,2} \cdot [M_1] \cdot [P_{p,q,n}]$
$Q_{p,q} + M_2 \rightarrow P_{p,q+1}$	$k_{p,2,2} \cdot [M_2] \cdot [Q_{p,q,n}]$	$Q_{p,q} + M_1 \rightarrow CD + U_{p,q}$	$k_{tm,2,1} \cdot [M_1] \cdot [Q_{p,q,n}]$
Spontaneous transfer ( $s^{-1}$ ) $P_{p,q,n} \rightarrow C^* + U_{p,q}$	$k_{f,1} \cdot [P_{p,q,n}]$	$Q_{p,q} + M_2 \rightarrow CD + U_{p,q}$	$k_{tm,2,2} \cdot [M_1] \cdot [Q_{p,q,n}]$
$Q_{p,q,n} \rightarrow C^* + U_{p,q}$	$k_{f,2} \cdot [Q_{p,q,n}]$	Termination with hydrogen ( $m^{0.5} \text{ mol}^{-0.5} s^{-1}$ ) $P_{p,q} + H_2 \rightarrow CD + U_i$	$k_{th,1} \cdot [H_2]^{0.5} \cdot [P_{p,q,n}]$
Transfer to monomer ( $m^3 \text{ mol}^{-1} s^{-1}$ ) $P_{p,q} + M_1 \rightarrow P_{1,0} + U_{p,q}$	$k_{fm,1,1} \cdot [M_1] \cdot [P_{p,q,n}]$	$Q_{p,q} + H_2 \rightarrow CD + U_i$	$k_{th,2} \cdot [H_2]^{0.5} \cdot [Q_{p,q,n}]$
$P_{p,q} + M_2 \rightarrow Q_{0,1} + U_{p,q}$	$k_{fm,1,2} \cdot [M_1] \cdot [P_{p,q,n}]$	Termination with organometallic ( $m^{0.5} \text{ mol}^{-0.5} s^{-1}$ ) $P_{p,q} + CC \rightarrow CD + U_{p,q}$	$k_{td,1} \cdot [CC]^{0.5} \cdot [P_{p,q,n}]$
$Q_{p,q} + M_1 \rightarrow P_{1,0} + U_{p,q}$	$k_{fm,2,1} \cdot [M_1] \cdot [Q_{p,q,n}]$	$Q_{p,q} + CC \rightarrow CD + U_{p,q}$	$k_{td,2} \cdot [CC]^{0.5} \cdot [Q_{p,q,n}]$
$Q_{p,q} + M_2 \rightarrow Q_{0,1} + U_{p,q}$	$k_{fm,2,2} \cdot [M_1] \cdot [Q_{p,q,n}]$	Spontaneous deactivation ( $s^{-1}$ ) $C^* \rightarrow CD$	$k_d \cdot [C_n^*]$

**Table 3**  
Correlations dependent on unknown parameters.

Properties	Correlation
Melt Index (g/(10 min))	$MI = \theta_{M,1} \cdot (\overline{MW}_w)^{-\theta_{M,2}}$
Density ( $\text{kg m}^{-3}$ )	$DS = \theta_{D,1} + \theta_{D,2} \cdot \log MI + \theta_{D,3} \cdot \delta^{\theta_{D,4}}$
Viscosity of the polymeric solution ( $\text{kg m}^{-1} s^{-1}$ )	$\mu = \theta_{V,1} \cdot (\overline{MW}_w)^{\theta_{V,2}}$
Specific heat of the polymeric solution ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$C_p = \theta_{C,1} T^2 + \theta_{C,2} T + \theta_{C,3}$
Mixing model for the non-ideal CSTR (kg/s)	$B = \frac{\rho \cdot V}{\mu} \cdot (\theta_{B,1} + \theta_{B,2} \cdot Rot + \theta_{B,3} \cdot W)$

**Fig. 2.** Illustration of the Gram-Schmidt orthogonalization.

Adapted from: Kravaris et al. (2013).

dependence between parameters. It is well suited for the problem of estimability, since it involves the matter of linearly dependence.

Previous works demonstrate the efficiency of the orthogonalization method, which can outperform other techniques such as the eigenvalue based method and the principal component analysis (Benyahia et al., 2013; Kravaris et al., 2013; Lund and Foss 2008; Quaiser and Mönnigmann 2009; Yao et al., 2003). These works demonstrate that the orthogonalization method is able to

simplify the problem of parameter estimation without excessively reducing the number of parameters to be estimated. Quaiser and Mönnigmann (2009), for example, apply the orthogonalization method to a mathematical model with 52 parameters, observing that three parameters would not be estimable.

According to Yao et al. (2003), the first step of the estimability analysis and ranking based on orthogonalization method is the definition of the sensitivity matrix. Consider the mathematical model of the process represented by:

$$\mathbf{y} = \mathbf{f}(\mathbf{x}(t), \boldsymbol{\theta}, t) \quad (2)$$

where  $\mathbf{y}$  is the vector with the model outputs,  $\mathbf{x}$  is the state vector,  $\boldsymbol{\theta}$  is the vector with the model parameters and  $t$  is the time. The coefficients of the sensitivity matrix are calculated by:

$$s'_{i,p} = \frac{\partial y_i}{\partial \theta_p} \bigg|_{t=t_n} \quad p = 1, 2, 3, \dots, n_p; i = 1, 2, 3, \dots, n_y; n = 1, \dots, n_t; \quad (3)$$

where  $y_i$  is the  $i$ -th output evaluated by the model,  $\theta_p$  is the  $p$ -th parameter,  $n_p$  is the number of parameters,  $n_y$  is the number of output variables,  $t_n$  is the time instant evaluated and  $n_t$  is the timeframe considered. The coefficients are normalized due to the different magnitude orders of the parameters and the model outputs (Yao et al., 2003; Lund and Foss 2008; Benyahia et al., 2013).



For a system with  $n_y$  outputs and  $n_p$  parameters, the sensitivity matrix of the model can be presented by:

$$\mathbf{S} = \begin{bmatrix} s'_{1,1}|_{t_1} & \cdots & s'_{1,n_p}|_{t_1} \\ \vdots & \ddots & \vdots \\ s'_{1,1}|_{t_n} & \cdots & s'_{1,n_p}|_{t_n} \\ \vdots & \vdots & \vdots \\ s'_{n_y,1}|_{t_1} & \cdots & s'_{n_y,n_p}|_{t_1} \\ \vdots & \ddots & \vdots \\ s'_{n_y,1}|_{t_n} & \cdots & s'_{n_y,n_p}|_{t_n} \end{bmatrix}_{n_y \times n_t \times n_p} \quad (4)$$

where each column of the matrix presents the influence of a certain parameter and each row represents the output  $y_i$  at each time instant  $t_n$ .

The magnitude of a column  $p$  is computed by:

$$\mathbf{M}(p) = \mathbf{S}_p^T \mathbf{S}_p \quad p = 1, \dots, n_p \quad (5)$$

where  $\mathbf{S}_p$  is the  $p$ -th column of the sensitivity matrix. The most estimable parameter corresponds to the column with the highest magnitude,  $\mathbf{SS}$ . The sensitivity matrix,  $\mathbf{S}$ , is then orthogonalized in relation to  $\mathbf{SS}$  (Yao et al., 2003), obtaining:

$$\mathbf{S}' = \mathbf{SS}(\mathbf{SS}^T \mathbf{SS})^{-1} \mathbf{SS}^T \mathbf{S} \quad (6)$$

The residual matrix is then computed. Since the orthogonal projection of a vector onto itself is the own vector, the column with the higher magnitude will be the same after orthogonalization and the corresponding residual will be zero, indicating which parameter has the highest effect on the process output. The magnitudes of the residual matrix are computed and the procedure continues until the higher magnitude is smaller than a cut-off value,  $c$ . Several works evaluate the influence of the cut-off value on the sensitivity analysis and on the ordenation of parameters, demonstrating that the smaller this value is, the more parameters will be selected as estimable (Kou et al., 2005; Quaiser and Mönnigmann, 2009). At the end, the estimability analysis presents the estimable parameters in descending order of influence on the model output. The other parameters, indicated as non-estimable, become constant at their initial estimate because they do not affect the model outputs as the orthogonalization analysis indicates. Fig. 3 resumes the algorithm of the orthogonalization method. For a better understanding, this algorithm is applied to a small example with 6 parameters and each step is detailed in the Appendix A.

If there are correlated parameters among the chosen set of estimable ones, they cannot be estimated simultaneously. Therefore, it is important to ensure that there are no correlations. The orthogonalization method proposed by Yao et al. (2003), as presented, identifies correlations between parameters. The authors argue that, because the orthogonalization method is a sequential rather an iterative procedure, it will always lead to a unique set of estimable parameters, even when the parameters are highly correlated, unless there is one or more exact linear relationships among the parameters. Any exact linear relationships could be detected with an eigenvalue-eigenvector analysis.

The estimability analysis yields the set of parameters which have to be estimated by the optimization. In order to evaluate the existence of the global optimum, the Hessian matrix and its eigenvalues should be analyzed. When the objective function is given by

the nonlinear least squares, the Hessian matrix might be computed according to (Bard, 1974):

$$H_{\alpha\beta} = 2 \sum_{\mu=1}^{n_y} \left( \frac{df_{\mu}}{d\theta_{\alpha}} \right) \left( \frac{df_{\mu}}{d\theta_{\beta}} \right), \quad \alpha, \beta = 1, 2, 3, \dots, n'_p \quad (7)$$

where  $n'_p$  is the number of estimable parameters. The derivatives in Eq. (7) are the elements of the sensitivity matrix  $\mathbf{S}_f$ , which is calculated by Eq. (4) and formed by the set of parameters indicated as estimable by the orthogonalization method. Therefore, the Hessian matrix, in matrix notation, is given by:

$$\mathbf{H} = 2\mathbf{S}_f^T \mathbf{S}_f \quad (8)$$

Since the matrix  $\mathbf{S}_f$  represents the search space formed by the decision variables, the hessian matrix indicates if a global optimum is to be found. If the hessian matrix is positive definite, there is a unique set of optimal parameters ( $\theta^*$ ), hence there is no linear relationships among the parameters. Otherwise, there is no mathematical guarantee that the optimization problem will find a minimum. If this happens, the search space is not strictly convex and the estimation might find a local minimum. Then, the estimability analysis has to be repeated after the parameter estimation in order to verify if the parameters converge to their final estimates, i.e. until their optimal values do not change significantly in this iterative procedure.

Although Yao et al. (2003) suggests analyzing the Hessian matrix, they do not evaluate it, so that the existence of the global optimum is not guaranteed. The computation of the eigenvalues of the Hessian matrix, as carried out here, further indicates the existence of a global minimum in the space formed by the estimable parameters. The estimability analysis performed in this work is then able to: eliminate possible correlations between the parameters; analyze the influence of each parameter in the response of the model; select the parameters with the highest influence on model outputs; reduce the number of parameters to be estimated; indicate the estimability of the selected parameters.

#### 4. Optimization problem formulation

The objective function of the parameter estimation problem is based on the maximum likelihood function:

$$\Phi = P(\mathbf{z}^e, \mathbf{z}^m, \omega_{zz}) \quad (9)$$

where  $\mathbf{z}^e$  is the set of experimental data,  $\mathbf{z}^m$  is the prediction of the model,  $\omega_{zz}$  is the uncertainty of the experimental data and  $P$  is the probability of the experimental data to coincide with the measured data under the uncertainty. The function aims to maximize the probability of the experimental data to coincide with the measured data. The following hypothesis can be assumed: the model is perfect; the measurement of the independent variables is not influenced by the measurement of the dependent variables; the probability distributions of the experimental deviations are Gaussian; the successive measurements of the independent and dependent variables are not correlated; the uncertainty associated with the measurement of the independent variables is negligible when taking into account the uncertainty of the measurement of the dependent variables; the uncertainty associated with the measurement of the dependent variables is constant. Therefore, the maximum likelihood function (8) turns out to be the least squares method (Bard, 1974).

By applying the least squares method (LSM) on the parameter estimation problem, it is possible to formulate a generic objective

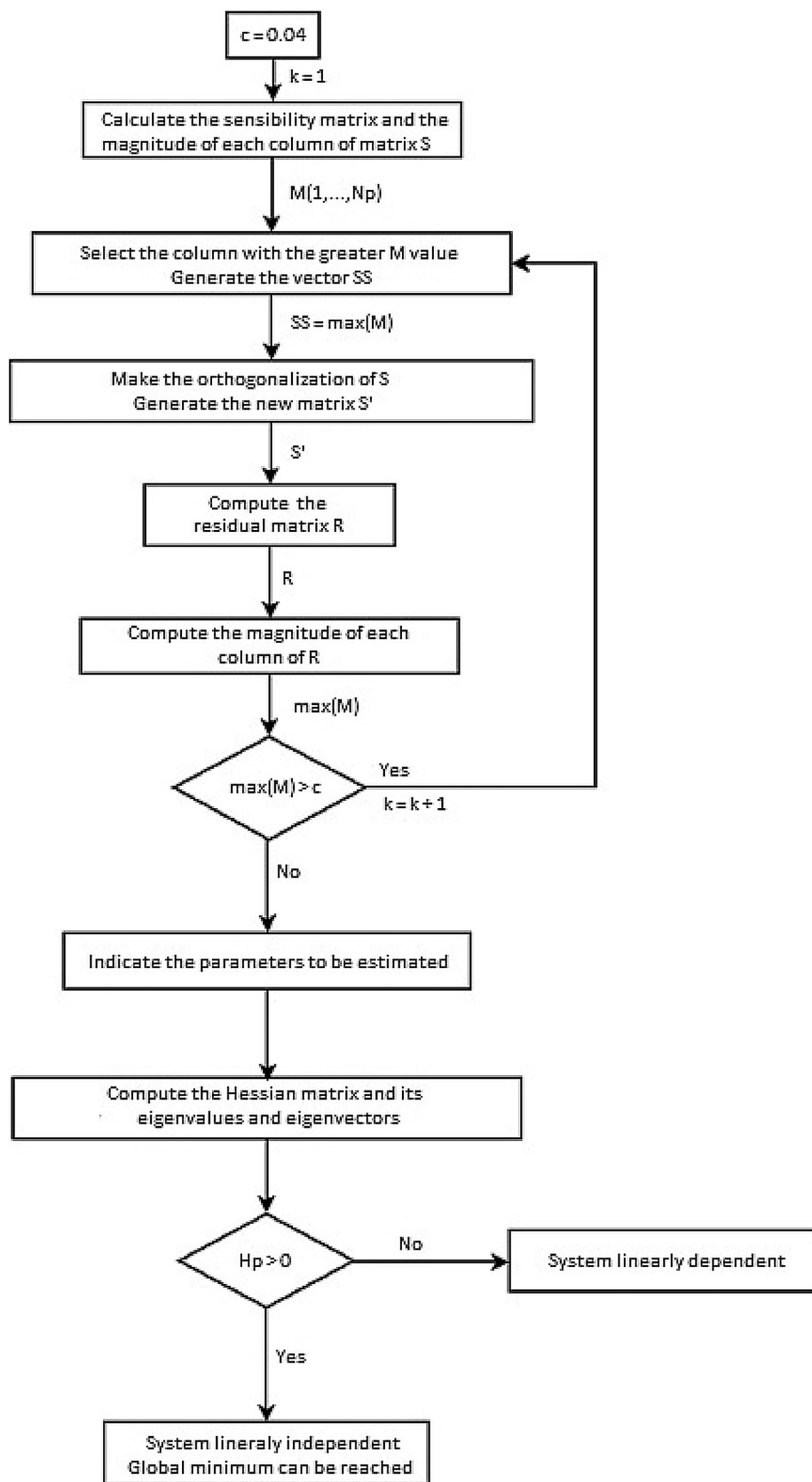


Fig. 3. Algorithm for the orthogonalization method with Hessian matrix analysis.

function. Then the optimization problem is formulated according to:

$$\min_{\theta} \sum_{j=1}^{n_y} \sum_{i=1}^{n_{pt}} \left( \frac{1}{u_{i,j}} \cdot \frac{\hat{y}_{i,j} - y_{i,j}}{y_{i,j}} \right)^2 \quad (10)$$

s.t.:

$$f(\theta, \mathbf{y}) = 0$$

$$g(\theta, \mathbf{y}) < 0$$

where  $\hat{y}_j$  and  $y_{i,j}$  are the predicted and measured output, respectively,  $\theta$  are the parameters to be estimated, which are normalized,  $u_{i,j}$  is the uncertainty of the  $i$ -th measurement of output  $j$ ,  $n_{pt}$  is the number of experimental data points,  $n_y$  is the number of evaluated outputs,  $\mathbf{f}$  represents equality constraints, which is given by the reactor model, and  $\mathbf{g}$ , the inequality constraints, such as bounds on the parameters. It was not possible to ascertain the measurement uncertainty since the industry did not provide the instrument's data sheet. The uncertainties  $u_{i,j}$  are considered then equal to unit. The process dynamics is also considered in the optimization problem. Since the model of the copolymerization reactor (Pontes et al., 2010) represents the system dynamics, the measurements  $i = 1, \dots, n_{pt}$  should follow this dynamic. For a given input condition, the DAE system is integrated and the objective function is computed.

The parameter estimation was carried out in three steps. Firstly, the kinetic constants were estimated together with physical and transport parameters (specific heat, mixing rule and viscosity) which were indicated as estimable by the estimability analysis. The output variables include temperatures and polymer production rate. Secondly, the parameters of the polymer properties were estimated, fixing the other parameter at the value obtained at the first step. At this step, melt index and density are the output variables. Lastly, all the estimable parameters were estimated, using the previous results as initial guess and all the measured outputs. This sequential procedure aims to improve the convergence of the optimization problem and to provide smaller deviations between measurements and predicted values.

The resulting problem is a NLP (*Non Linear Programming*) since the process model is highly nonlinear. The numerical solution was carried out by the functions E04UEF and E04UCF, based on the SQP (*Successive Quadratic Programming*) algorithm and available at the NAG library (*Numerical Algorithm Group*) for Fortran (The Numerical Algorithms Group Limited, 2015). The optimization took roughly 30 h to run in an Intel Core i5, Quad Core, 8 Gb of RAM.

## 5. Results and discussions

This section presents the results obtained from the estimability analysis, indicating which parameters have to be estimated by the optimization problem, as well as the results of the parameter estimation. A comparison between the model prediction and the experimental data (estimation and validation data sets) is provided in order to verify the quality of fit of the adjusted model.

### 5.1. Estimability analysis

The algorithm depicted in Fig. 3 indicates that the cut-off value is the stopping criterion of the estimability analysis. The lower the cut-off value is, the greater will be the number of parameters ranked. As mentioned by Yao et al. (2003), the choice of the stopping criterion is an arbitrary question but depends on the level of noise of the experiment. A higher cut-off value is recommended for high noise levels or when the model structure is imperfect. Therefore, it is important to evaluate the sensitivity of the estimability analysis

**Table 4**  
Effect of the cut-off value on the parameters ranked.

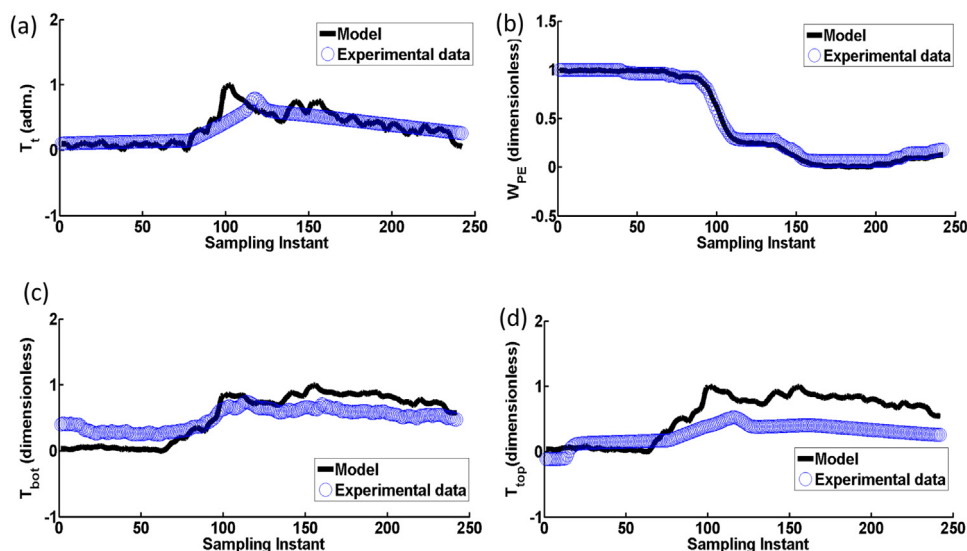
Name <sup>[1]</sup>	Rank			Optimal value
	$c = 0.4$	$c = 0.04$	$c = 0.004$	
$\theta_{V,1}$	1	1	1	1.33E+00
$\theta_{C,2}$	2	2	2	7.56E+01
$\theta_{M,2}$	3	3	3	1.00E+00
$\theta_{M,1}$	4	4	4	3.11E+07
$\theta_{V,2}$	5	5	5	2.11E-05
$E_{p,1,1}$	6	6	6	2.24E+04
$E_{f,1}$	7	7	7	5.90E+04
$\theta_{C,3}$	8	8	8	-1.50E+04
$\theta_{D,1}$	9	9	9	9.59E-01
$E_{t,1}$	10	10	10	3.91E+04
$E_{p,1,2}$	11	11	11	3.02E+05
$E_{f,2}$	12	12	12	5.23E+05
$E_{fm,1,1}$	13	13	13	3.17E+04
$E_{t,2}$	14	14	14	3.16E+04
$E_{p,2,2}$	15	15	15	2.93E+04
$E_{it,1}$	16	16	16	3.91E+04
$E_D$	17	17	17	3.91E+04
$E_{\beta,1}$	18	18	18	3.17E+04
$E_{\beta,1}$	19	19	19	3.17E+05
$E_{p,2,1}$	20	20	20	2.41E+04
$E_{fm,1,2}$	21	21	21	2.58E+04
$E_{tm,2,1}$	-	22	22	1.54E+04
$A_{f,1}$	-	23	23	5.94E+04
$\theta_{D,2}$	-	24	24	8.53E-03
$\theta_{B,1}$	-	25	25	1.24E+00
$\theta_{D,4}$	-	26	26	1.05E+00
$\theta_{D,3}$	-	27	27	-6.00E-01
$\theta_{B,3}$	-	28	28	1.00E+00
$\theta_{B,2}$	-	29	29	1.50E-03
$A_{fm,1,2}$	-	-	30	-
$A_{tm,1,2}$	-	-	31	-
$A_{p,1,1}$	-	-	32	-

results regarding the cut-off value. Three different cut-off values are compared for this case study: 0.4; 0.04 and 0.004. The parameter's values reported by Pontes et al. (2010) are taken as starting point for the estimability analysis. Table 4 presents the results, i.e., the parameters ranked, for each cut-off value.

When  $c = 0.4$ , the coefficients of the polymer density correlation are not ranked. A slight variation of  $10^{-3}$  in the polymer density might significantly change the polymer end-use properties so that another polymer grade might result. The parameters  $\theta_{D,2}$ ,  $\theta_{D,3}$  and  $\theta_{D,4}$  control this slight change therefore should be estimated for a better description of the polymer density. They might not have been ranked due to the small magnitude of the density variation compared with other output variables when computing the sensibility matrix. The normalization imposed by Eq. (3) does not avoid this problem since the coefficient of the sensibility matrix is divided by the nominal value of the output variable, not its variation.

When  $c = 0.04$  or  $c = 0.4$  the set of estimable kinetic parameters contains solely one frequency factor ( $A_{f,1}$ ), probably because it is the greatest one, and several activation energy parameters. The estimability analysis, then, indicates that the frequency factors are correlated with the activation energy. For the smallest cut-off value, then, it seems that the algorithm starts selecting variables correlated with variables already ranked. The cut-off value  $c = 0.04$  is therefore chosen so that 29 parameters from the 68 have to be estimated. These estimable parameters become the decision variables in the optimization problem.

It is important to investigate the consistence of the set of selected parameters in Table 4. The main reactions in the kinetic mechanism are present among the ranked parameters, i.e. the propagation, deactivation, spontaneous transfer, spontaneous termination and transfer with hydrogen, responsible for controlling the molecular weight. The monomer (1) is more reactive than the comonomer (2), so it is expected that the kinetic parameters of the



**Fig. 4.** Comparison between the model prediction and process data (estimation data set): (a) PFR outlet temperature  $T_t$ ; (b) Production rate,  $W_{PE}$ ; (c) CSTR bottom temperature  $T_{bot}$ ; (d) CSTR top temperature,  $T_{top}$ .

reactions with a terminal monomer (1) have a greater effect on the process outputs. This is in accordance with the results of the estimability analysis since the ranked activation energies of the transfer reactions with monomer, hydrogen and organometallic correspond to the terminal monomer (1). The parameters of the mixing rule, specific heat and viscosity correlations are ranked as expected since they influence the reaction temperature. Furthermore, the parameters of the melt index and density correlations are also ranked since they correlate with the polymer quality.

In order to verify if the space formed by the final set of parameters is strictly convex, the eigenvalues and eigenvectors of the Hessian matrix were computed. The results show that the space is not strictly convex, therefore the optimization might lead to a local minimum and consequently the estimation will have to be carried out carefully. After the parameter estimation, presented in the next section, the estimability analysis was repeated with the optimum values as starting point. This analysis gives the same ranking illustrated in Table 4 ( $c = 0.04$ ). The eigenvalues analysis, though, indicate that the Hessian is positive definite. This leads to the conclusion that the parameter estimation was successful and the optimum is not local.

## 5.2. Parameter estimation

In order to have a reasonable initial guess to the parameter estimation, a previous optimization with all the 68 parameters was carried out, taking the values reported by Pontes et al. (2010) as initial guess. The initial guess to the additional kinetic constants for the termination reactions were taken from preliminary parameter estimation based on stationary synthesis conditions. It is important to mention that this estimation yielded deviations greater than 25% between the predicted and experimental values and could not predict the polymer properties. This indicates the benefits of the estimability analysis as it allows much lower deviations, as will be detailed next.

The optimization computed the optimal value of 29 estimable parameters, given in Table 4. The initial guess was kept for the parameters which were not estimated. The final values of the parameters were analyzed and they are in accordance with the expected phenomenological behavior. Since monomer type 1 is more reactive than monomer type 2, reactions with monomer 1

( $M_1$ ) should occur more easily than with monomer type 2 ( $M_2$ ). Accordingly, reactions with a terminal monomer type 1 ( $P_{p,q}$ ) should occur more easily than with a terminal monomer type 2 ( $Q_{p,q}$ ). This is observed if we analyze the activation energies together with the frequency factors. A table with the values of all parameters (optimal and initial guess if not estimable) is provided in the Supplementary material for the more interested readers.

Fig. 4 compares the model prediction with the process data (estimation set): PFR outlet temperature, production rate, CSTR bottom and top temperatures. All the values presented are normalized due to confidentiality reasons. The model can follow the process dynamics reasonably well with small maximum relative deviations: 2.0% for the production rate, 2.4% for PFR outlet temperature, 2.5% and 3.0% for the CSTR bottom and top temperatures, respectively. Despite the small deviation, the top temperature ( $T_{top}$ ) seems to be overestimated. According to practitioners at industry, the polymer deposits on the thermocouples inside the CSTR reactor, damaging the temperature measurements. The good model fit for the PFR outlet temperature and for the polymer production rate reinforces this affirmation.

Fig. 5 illustrates the model fit of the polymer properties, MI and density, after the parameter estimation. The prediction of the MI presents a maximum relative deviation of 16%, observed during the transition. As discussed before, the measurements are associated with large dead times and the sampling frequency is very low (higher than 60 min), so that the last measurement is repeated until the next becomes available. Therefore, the dynamic behavior of the system is not represented by the measurements carried out in laboratory. Between time instants 100–150, when the deviation between the model prediction and experimental data is higher, there is no measurement and the experimental value in Fig. 5 corresponds to the last measurement. After time instant 150, though, the model prediction fits reasonably well the new experimental data with a maximum deviation of 8.2%. For the polymer density, the maximum deviation observed was of 0.3%.

In the absence of measurements of the polymer properties during a large time interval, the input variables (Fig. 6) might be evaluated in order to ascertain if the model can predict the dynamic behavior of the system. Fig. 6a indicates that at time instant 105 there is a sudden increase in the hydrogen inlet concentration, followed by smaller steps after time instant 120. This adjustment is



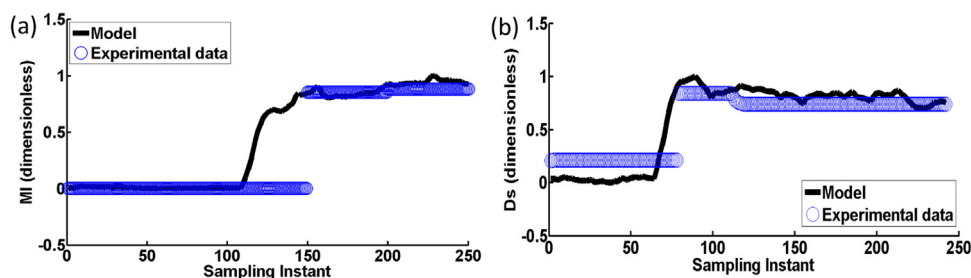


Fig. 5. Comparison between the model prediction and process data (estimation data set): (a) Melt Index, MI; (b) Density, Ds.

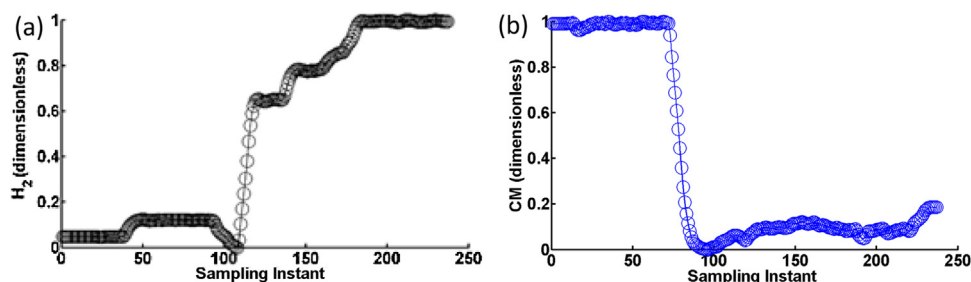


Fig. 6. Experimental data for (a) hydrogen,  $H_2$  and (b) comonomer, CM inlet concentrations (estimation data set).

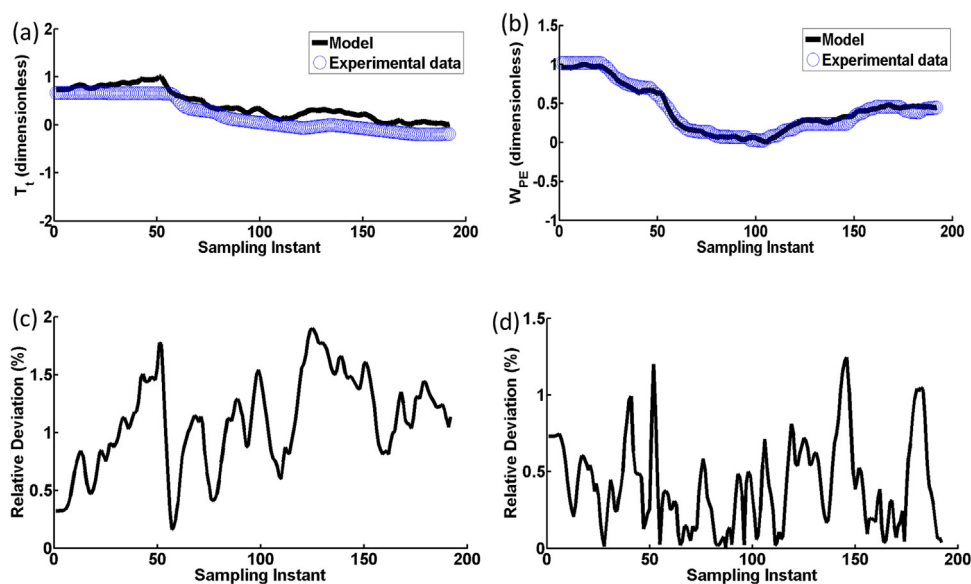


Fig. 7. Comparison between the model prediction and process data (validation data set): (a) PFR outlet temperature  $T_f$ ; (b) Production rate,  $W_{PE}$ . Relative deviation of (c) PFR outlet temperature and (d) Production rate.

carried out manually by process operators in order to adjust the MI to the next polymer grade. As Fig. 5a illustrates, the predicted MI follows a similar behavior of the hydrogen inlet concentration to reach the next polymer grade, indicating that the model is able to predict not only the stationary condition but also the dynamics of the MI. Fig. 6b shows that at time instant 65 there is a sudden decrease in the comonomer inlet concentration, what is supposed to increase the polymer density. Fig. 5b confirms that the model is also able to represent the dynamics of the density reasonably well.

All the data was obtained from industry, but the instrument and measurement uncertainty was not provided. A question that may arise, then, is how the measurement uncertainty can influence the results obtained. A detailed analysis is out the scope of this work but a brief assessment is given next.

In order to ensure the quality of the model fitting, it is necessary to validate the model at another operating condition, i. e., with a data set different from the one used for estimation. This is especially true for the case study because the estimability analysis indicated that the estimation might lead to a local minimum, what would compromise the quality of the model fitting. Figs. 7 and 8 compares the model prediction with the process data for the validation data set. The maximum relative deviations are 1.2% for the PFR outlet temperature, 1.9% for the production rate, 1.3% and 4.8% for the CSTR bottom and top temperatures, respectively. The profiles indicate that the model is also able to predict the dynamic of these variables reasonably well. The CSTR top temperature seems to be overestimated, as observed for the estimation data set. Accordingly, the deviation is more pronounced for higher melt index values (Figs. 5 and 9), i.e., for shorter polymer chains. The predictions of the

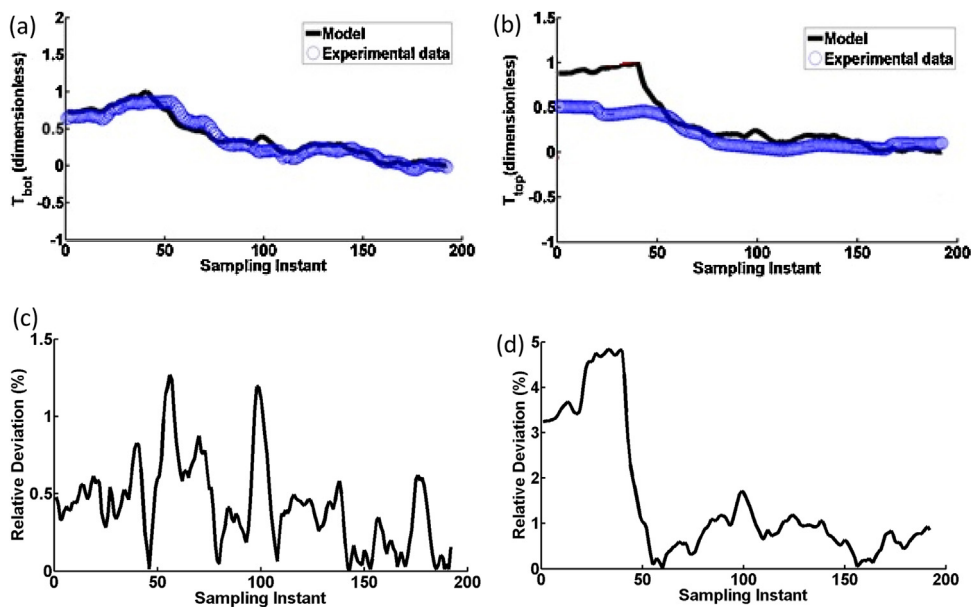


Fig. 8. Comparison between the model prediction and process data (validation data set): (a) CSTR bottom temperature,  $T_{bot}$ ; (b) CSTR top temperature,  $T_{top}$ . Relative deviation of (c) CSTR bottom temperature and (d) CSTR top temperature.

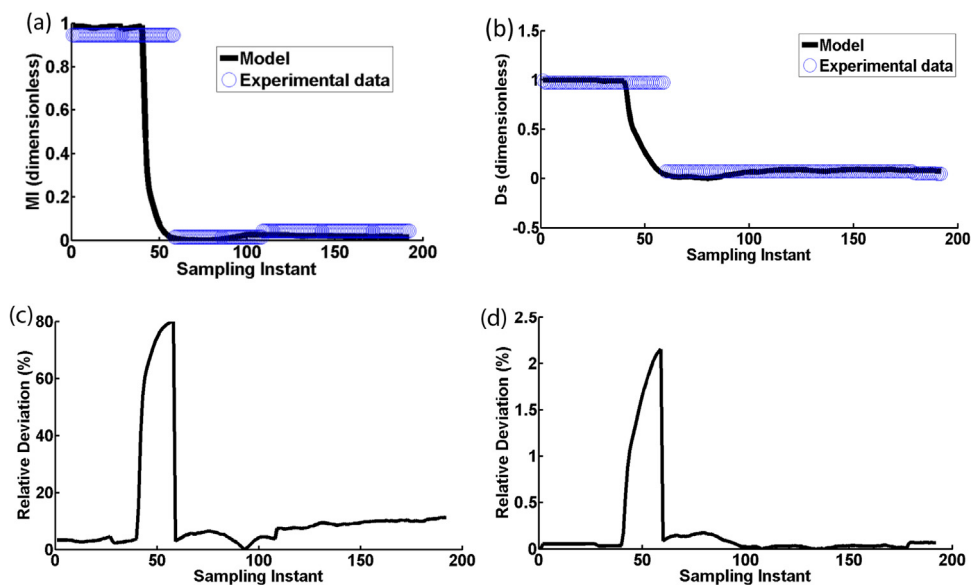


Fig. 9. Comparison between the model prediction and process data (validation data set): (a) Melt Index, MI; (b) Density,  $D_s$ .

other output variables confirm the quality of fit of the model, indicating that the temperature measurements inside the CSTR might have a higher uncertainty due to the deposition of polymer on the thermocouples.

The model is also able to predict with precision the stationary and dynamic conditions of the polymer properties, as illustrated in Figs. 9 and 10. As before, the larger deviations occur during the transitions, when there is no measurement available. However, the profiles of the polymer properties, MI and density, follow a dynamics similar to that presented by the input variables, indicating that the model is indeed validated.

## 6. Conclusion

This paper presents how the estimability analysis allows parameter estimation simplification of a complex phenomenological

model representing an industrial scale process. Previous studies in literature have already dealt with the preliminary analysis of the parameters, but they use experimental data obtained from laboratory or pilot plants. Using experimental data obtained from process history presents some challenges not faced with laboratory or pilot plant experiments: less information is available, the measurements have more uncertainties and the experiments might not be designed.

The estimability analysis based on the orthogonalization method allowed determining the set of estimable parameters of a phenomenological model representing an industrial scale copolymerization process. The number of parameters to be estimated was reduced from 68 to 29, ensuring a successful estimation. The Hessian matrix analysis indicates that the space formed by these parameters is not strictly convex, hence a local minimum might be found. The estimability analysis was then repeated, indicating

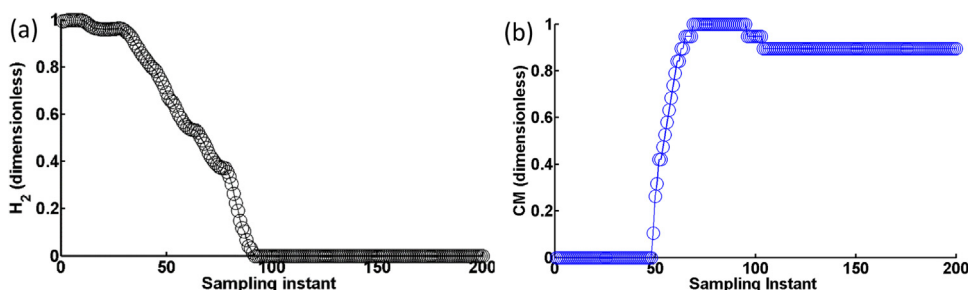


Fig. 10. Experimental data for (a) hydrogen, H<sub>2</sub> and (b) comonomer, CM inlet concentrations (validation data set).

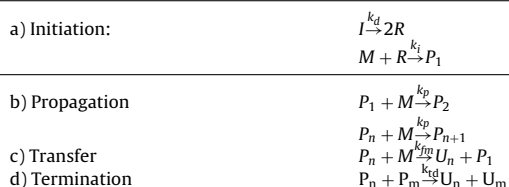
a positive definite Hessian matrix. The parameter estimation was followed by the model validation with a different data set, representative of another polymer grade. The small deviations between the model prediction and the experimental data, both from the estimation and validation data sets, indicate the quality of fit of the model.

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### Appendix A.

This appendix demonstrates the orthogonalization method for estimability analysis, described in Section 3, with a small example. The case study is a batch reactor where a free radical polymerization takes place, according to the kinetic mechanism:



where  $I$  is the initiator,  $M$  the monomer,  $R$  the free radical,  $P_i$  the live polymer chain with length  $i$ ,  $U_i$  the dead polymer chain with length  $i$ ,  $k$  is the kinetic constant and the subscripts  $d$ ,  $p$ ,  $fm$  and  $td$  correspond the initiation, propagation, transfer and termination reactions respectively.

The following hypotheses are assumed: the reaction takes place in solution but there is no transfer with solvent; the process is isothermal; the QSSA (*Quasi-Steady State Assumption*) is assumed for the live polymer chains. The mass balance then yields the model:

$$\frac{dI}{dt} = -k_d \cdot I \quad (A1)$$

$$\frac{dR}{dt} = -k_i \cdot M \cdot R + 2 \cdot f \cdot k_d \cdot I \quad (A2)$$

$$\frac{dM}{dt} = -k_i \cdot M \cdot R - k_p \cdot M \cdot \mu_0 - k_{fm} \cdot M \cdot \mu_0 \quad (A3)$$

$$\frac{d\gamma_0}{dt} = k_{fm} \cdot M \cdot \mu_0 + k_{td} \cdot \mu_0 \cdot \mu_0 \quad (A4)$$

$$\frac{d\gamma_1}{dt} = k_{fm} \cdot M \cdot \mu_1 + k_{td} \cdot \mu_0 \cdot \mu_1 \quad (A5)$$

$$\frac{d\gamma_2}{dt} = k_{fm} \cdot M \cdot \mu_2 + k_{td} \cdot \mu_0 \cdot \mu_2 \quad (A6)$$

Table A1  
 Initial estimates of the parameters.

Specie	Value	Units
$k_d$	9,70E-06	l/mol h
$k_p$	9,55E+02	l/mol h
$k_i$	9,55E+02	l/mol h
$k_{fm}$	1,00E-08	l/mol h
$k_t$	2,04E+06	l/mol h
$f$	7,00E-03	l/mol h

$$\mu_0 = \left( \frac{k_i \cdot M \cdot R}{k_{td}} \right)^{1/2} \quad (A7)$$

$$\mu_1 = \frac{k_i \cdot M \cdot R + k_p \cdot M \cdot \mu_0 + k_{fm} \cdot M \cdot \mu_0}{k_{td} \cdot \mu_0 + k_{fm} \cdot M} \quad (A8)$$

$$\mu_2 = \frac{k_i \cdot M \cdot R + k_p \cdot M \cdot 2 \cdot (\mu_1 + \mu_0) + k_{fm} \cdot M \cdot \mu_0}{k_{td} \cdot \mu_0 + k_{fm} \cdot M} \quad (A9)$$

where  $f$  is the efficiency factor,  $\mu_i$  and  $\gamma_i$  are the  $i$ -th order moments of the distribution of the live and dead polymer, respectively.

The average numerical ( $M_n$ ) and mass ( $M_w$ ) molecular weights and the polydispersity ( $P_d$ ) are computed by:

$$M_n = \frac{\gamma_1}{\gamma_0} \quad (A10)$$

$$M_w = \frac{\gamma_2}{\gamma_1} \quad (A11)$$

$$P_d = \frac{M_w}{M_n} \quad (A12)$$

The parameters to be estimated are the kinetic constants of dissociation, propagation, initiation, transfer with monomer, termination and the efficiency factor:

$$\theta = [k_d \quad k_p \quad k_i \quad k_{fm} \quad k_t \quad f]^T \quad (A13)$$

The estimability analysis is then carried out in order to assert which of these parameters have to be estimated. The initial estimates of the parameters are given in Table A1 and a cut-off value  $c = 0.004$  is assumed. The initial condition of the polymerization is given by  $R_0 = 0$  g/L,  $M_0 = 0.033$  g/L,  $I_0 = 3.66$  g/L,  $\mu_{i,0} = \gamma_{i,0} = 0$ ,  $i = 1, 2, 3$ .

The sensitivity matrix is then computed according to Eq. (3):

$$S = \begin{bmatrix} -0.3743 & 0.9993 & -0.0000 & -0.0000 & -0.3845 & -0.3765 \\ 0.3047 & 0.9999 & -0.0001 & 0.0000 & -0.3340 & -0.3062 \\ 0.0699 & 0.0006 & -0.0000 & 0.0000 & 0.0500 & 0.0704 \end{bmatrix} \quad (A.14)$$

where the column represents the parameter  $p$  and the row, the process outputs  $y = [M_n \quad M_w \quad P_d]$ .

The magnitude of each column is computed according to Eq. (5). Table A2 shows the magnitude values  $M(p)$  of each iteration. It indicates that, at the first iteration, the second column is the one with

**Table A2**  
Magnitudes at each iteration.

Iteration	$k_d$	$k_p$	$k_i$	$k_{fm}$	$k_t$	$f$
1	0.0077	1.99823	7,83E-09	1.46E-15	0.23	0.24
2	7.51E-05	2.47E-32	2.51E-09	5.00E-17	0.0073	0.0074
3	7.51E-05	2.47E-32	2.51E-09	5.00E-17	6.23E-08	2.98E-31

the highest magnitude,  $SS$ . The sensitivity matrix is then orthogonalized in relation to the column  $SS$ , as Eq. (6) indicates, and the residual matrix is computed, yielding:

$$R = \begin{bmatrix} -0.0349 & 0.0000 & 0.0000 & -0.0000 & -0.0254 & -0.0353 \\ 0.0349 & 0.0000 & -0.0000 & 0.0000 & 0.0253 & 0.0352 \\ 0.0701 & 0.0000 & -0.0000 & 0.0000 & 0.0502 & 0.0706 \end{bmatrix} \quad (A15)$$

The column with the highest magnitude, corresponding to  $k_p$  assumes residual values equal zero, as expected. The magnitudes of the residual matrix are then computed. At the second iteration the efficiency factor is chosen as the second most important parameter of the model. Since the highest magnitude is lower than the cut-off value, the analysis stops. This case study shows that the orthogonalization method can rank the model parameters, reducing the number of parameters to be estimated from six to two.

The magnitude of the kinetic constant of dissociation (first column) varies significantly from the first to the second iteration, indicating that this parameter is much correlated with the kinetic constant of propagation. The same can be observed for  $k_t$  from the second to the third iteration, indicating that this parameter is much correlated with the efficiency factor.

Finally, the hessian matrix is computed according to Eq. (8) in order to verify the estimability of the space formed by the two parameters ranked. It is given by:

$$H = \begin{bmatrix} 3.996 & -1.364 \\ -1.364 & 0.4808 \end{bmatrix} \quad (A16)$$

The eigenvalues of the hessian are 0.0134 and 4.464. Therefore, the hessian matrix is positive definite. In this way, we can conclude that the space formed by the two parameters is convex and the global minimum is to be found in the estimation step.

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