

Process modeling strategy combining analytical and data based techniques – I. NN identification of reaction rates with known kinetics coefficients

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Abstract — This work deals with the fusion of the data-based and analytical submodels in the process engineering. In contrast to the traditional way of process reaction rates identification by an exhaustive and/or expensive search for the most appropriate parameterized structure, a neural network (NN) based procedure is developed here to identify the reaction rates in the framework of a first principles process model. Since the reaction rates are not measured variables a particular network training structure and algorithm are developed to make possible the supervised NN learning. Our contribution is focused on the general modeling of a class of nonlinear systems representing several industrial processes including crystallization and precipitation, polymerization reactors, distillation columns, biochemical fermentation and biological systems. The proposed algorithm is further applied for estimation of the precipitation rate of calcium phosphate and compared with alternative solutions.

I. INTRODUCTION

This paper is focused on issues of efficient modelling for a class of nonlinear systems arising as models for biochemical reactions. It is a contribution to the general process modelling by introducing an alternative hybrid modelling strategy combining analytical and data-based approaches. The new algorithm is illustrated for the benchmark example of calcium phosphate precipitation.

We consider a general reaction process modelled by ordinary differential equations of the following matrix form (Bastin and Dochain, 1990; Georgieva and Feyo de Azevedo, 2006)

$$\frac{dX}{dt} = K\varphi(X, T) + F_{in} - F_{out} \quad (1.1)$$

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$$\frac{dT}{dt} = K_0\varphi(X, T) + F_{in} - DT \quad (1.2)$$

where, for $n, m \in \mathbb{N}$, the constants and variables denote

$X = (x_1(t), \dots, x_n(t))^T$ concentrations of the n process variables at time t ;

T temperature of the reactor;

$K = [k_1, \dots, k_m] \in R^{n \times m}$ stoichiometric matrix-kinetics coefficients

$K_0 \in R_{\geq 0}^m$ coefficients of exothermicity;

$\varphi = (\varphi_1, \dots, \varphi_m)^T$ reaction rate vector, where
 $\varphi_j(\cdot, \cdot) : R_{\geq 0}^{n+1} \rightarrow R_{\geq 0}$ are locally Lipschitz continuous functions, $j=1, \dots, m$;

$F_{in}(\cdot) : R_{\geq 0} \rightarrow R_{\geq 0}^n$ piecewise continuous and bounded function of n feed concentrations at time t .
 $F_{in} = (F_1^{in}(t), \dots, F_n^{in}(t))^T$

$F_{out}(\cdot) : R_{\geq 0} \rightarrow R_{\geq 0}^p$ piecewise continuous and bounded function of n effluent concentrations at time t .
 $F_{out} = (F_1^{out}(t), \dots, F_p^{out}(t))^T$

D heat transfer rate

In reaction process systems, equations (1.1) and (1.2) usually represent the mass and energy balances, respectively. The first right-hand side terms describe the kinetics of chemical, biochemical or biological reactions i.e. the phenomena of transformation or conversion of one reaction component into another. The remaining right-hand side terms describe the transport dynamics of the components through the reactor. The class of nonlinear systems represented by (1) has been used extensively as models in several industries including crystallization and precipitation processes, polymerization reactors, distillation columns, biochemical fermentation and biological systems.

The reaction rate vector φ is a key parameter for the

description of all concentrations (e.g. chemical species growth, substrate consumptions, product formation). The traditional way for identification of φ is in the form of analytical deterministic expressions (Bastin and Dochain, 1990, Oliveira et al, 2002, Lubenova et al, 2003).

First, the parameterized structure of the reaction rate is determined based on data obtained by specially designed experiments. Then the respective parameters of this structure are estimated. This is a highly complex empirical procedure due to the strong nonlinear characteristics of the process reactions. Most of the parameter estimation techniques rely on the assumption that the proposed model structure is correct and theoretically identifiable (Walter and Pronzato, 1997). It is further assumed that the initial values of the identified parameters are close to the real process parameters (Noykove et al., 2002). The above assumptions are rather strong, they are usually valid for well known processes or after a great number of expensive laboratory investigations define the proper reaction rate model structure.

In this paper we introduce an alternative approach, based on relaxed assumptions. Instead of exhaustive search for the most appropriate parameterised reaction rate structure, a data-driven technique is applied to identify the reaction rates. In the present work a neural network (NN) is the selected modelling technique but other alternatives can be also considered. The NN reaction rate submodel is incorporated in the general dynamical model (1) and this mixed structure is termed knowledge-based hybrid model (KBHM), see Fig.1. A systematic procedure for the reaction rates identification is discussed in the next section.

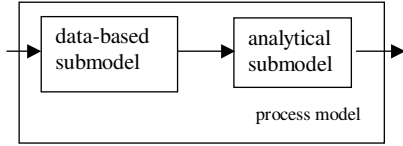


Fig. 1 Knowledge-based hybrid model (KBHM)

III. PROCEDURE FOR NN BASED IDENTIFICATION OF REACTION RATES

The process reaction rates are not measured variables and this turns out to be a basic obstacle for the application of any data-based modelling tools. Indeed, for the particular case of a NN, the supervised training requires an error signal between the network output and the corresponding target to update the network weights, but targets are not available. Therefore, we developed an alternative training procedure. The scenario is to propagate the network output through some part of the analytical (fixed) model until it arrives to an output for which data are available (see Fig.2). The proper choice of the partial analytical model and the formulation of the error signal for NN updating are discussed below.

Step 1: Model transformation

First, we make two principle assumptions for the general dynamical model (1):

(A1) Not all of the states of (1) are measured.

(A2) Only part of the states depend explicitly on a certain reaction rate φ_j .

(A3) All kinetics coefficients are known, that is the matrix K_{aug} is known.

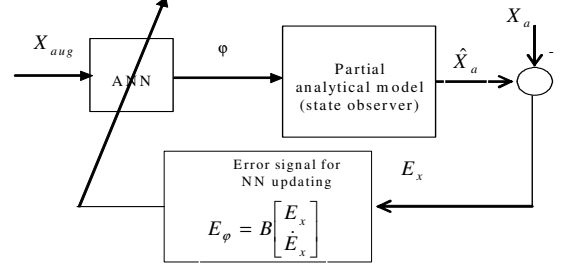


Fig.2. NN reaction rates identification with known K_{aug}

The intuition behind A1 and A2 is to formulate the task as general as possible and define a procedure suitable for a great number of particular situations.

Based on (1), and for more convenience, an augmented state vector is defined

$$X_{aug} = \begin{bmatrix} X \\ T \end{bmatrix}, K_{aug} = \begin{bmatrix} K \\ K_0 \end{bmatrix}, \dim(X_{aug}) = n + 1, \dim(K_{aug}) = (n + 1) \times m, \quad (2)$$

Then (1) is rewritten as

$$\frac{dX_{aug}}{dt} = K_{aug} \varphi(X_{aug}) - DX_{aug} + F_{in} - F_{out}. \quad (3)$$

According to A2, we assume that only part of the states, the subvector X_a , depends on a specific reaction rate φ_j .

Then

$$X_{aug} = \begin{bmatrix} X_a \\ X_b \end{bmatrix}, \text{ and}$$

$$\frac{dX_a}{dt} = K_a \varphi(X_a, X_b) - DX_a + F_{in_a} - F_{out_a} \quad (4)$$

$$\frac{dX_b}{dt} = K_b \varphi(X_a, X_b) - DX_b + F_{in_b} - F_{out_b} \quad (5)$$

Using linear algebra, a new vector Z of dimension $(n + 1 - l)$ is defined as the following linear combination of the state variables

$$Z = A_0 X_a + X_b, \quad (6)$$

where $\dim(X_a) = l$, $\text{rank}(K_{aug}) = l$, and matrix A_0 of dimension $(n+1-l) \times l$, is the unique solution of the equation

$$A_0 K_a + K_b = 0. \quad (7)$$

Thus, the general model (3) is equivalent to:

$$\frac{dX_a}{dt} = K_a \varphi(X_a, X_b) - DX_a + F_{in_a} - F_{out_a} \quad (8.1)$$

$$\frac{dZ}{dt} = -DZ + A_0(F_{in_a} - F_{out_a}) + (F_{in_b} - F_{out_b}) \quad (8.2)$$

The purpose of the model transformation (8) is twofold. On the one hand, we extract this part of the model that explicitly depends on φ , which responds to the assumption A2. On the other hand, the dynamics of Z are independent of φ and eq. (8.2) appears to be a convenient expression to recover the unmeasured states, which responds to the assumption A1. The procedure for state recovery, termed as state observer in the control theory, is discussed below.

Step 2: State observer

Let X_1, X_2 be the vectors of measured and unmeasured states, respectively. Then, we can rewrite vector Z as

$$Z = A_1 X_1 + A_2 X_2. \quad (9)$$

with appropriate definitions of matrices A_1 and A_2 . If matrix A_2 has a left inverse, the following observer follows from (8.2) and (9) (see Oliveira et al. 2002, for more details)

$$\frac{d\hat{Z}}{dt} = -D\hat{Z} + A_0(F_{in_a} - F_{out_a}) + (F_{in_b} - F_{out_b}) \quad (10.1)$$

$$\hat{X}_2 = A_2^{-1}(\hat{Z} - A_1 X_1) \quad (10.2)$$

where \hat{Z} and \hat{X}_2 denote estimates of Z and X_2 , respectively. The observer equation (10.1) can be interpreted as a copy of the model (8.2) with an extra term, proportional to the observation error of the measured part of the state ($X_1 - \hat{X}_1$). In case of perfect estimation this term is equal to zero. The matrix Ω is the design parameter which is commonly selected as

$$\Omega = \text{diag} \{-\omega_i\}, \quad \omega_i \in \Re^+, \quad i = 1..N \quad (11)$$

and several standard solutions like extended Luenberger observer or extended Kalman observer can be applied to

design it (Basten and Dochain, 1990).

Step 3: Error signal for NN updating

At the first step of the procedure, we transform the model (3) into the model (8), which is the basis for selection of the partial analytical model required in the hybrid structure of Fig. 2. At the second step, we determine a way how to get data for (how to estimate) all states Z . At this step we repeat the routine of step 2 only for the submodel (8.1). Hence, the following state observer is introduced as a partial analytical model in Fig. 2.

$$\frac{d\hat{X}_a}{dt} = K_a \varphi_{NN} - D\hat{X}_a + F_{in_a} - F_{out_a} - \Omega(X_a - \hat{X}_a). \quad (12)$$

Eq. (12) is used not to estimate the states (they were already estimated at the previous step) but to provide on-line information for the updating of the estimated reaction rate. Definitions for the observation error E_x and the error signal for NN updating E_φ are the following expressions:

$$E_x = (X_a - \hat{X}_a) \quad (13)$$

$$E_\varphi = \varphi(X_a, X_b) - \varphi_{NN} \quad (14)$$

Subtracting (8.1) from (12) we obtain

$$\frac{dE_x}{dt} = K_a E_\varphi - DE_x + \Omega E_x. \quad (15)$$

Rearranging (15) we get the following expression of the NN error signal that is suitable for on-line NN training and can be easily interpreted

$$E_\varphi = B \begin{bmatrix} E_x \\ \dot{E}_x \end{bmatrix}, \quad B = K_a^{-1} [D - \Omega \quad 1]. \quad (16)$$

The systematic procedure, presented in this section, is further tested for the estimation of the precipitation rate of calcium phosphate and is compared with alternative solutions.

IV. CASE STUDY – ESTIMATION OF THE PRECIPITATION RATE OF CALCIUM PHOSPHATE

The precipitation of calcium phosphate was studied by many authors under different conditions (Sorensen et al., 2000, Ferreira et al., 2003). Depending on the temperature, the level of supersaturation, pH and initial concentration of reagents, one can obtain different calcium phosphate phases. One of them is the dicalcium phosphate dihydrate (DCPD) known also as brushite. DCPD is recognized as an important product in the application of fertilizers to soil and is studied

mainly for its role in the physiological formation of calcium phosphates.

For the present study, the precipitation of DCPD was performed in a batch laboratory crystallizer. The precipitation was carried out by mixing equimolar quantities of calcium hydroxide suspension and orthophosphoric acid solution. Five successive stages were identified during a number of experiments performed with different initial reagent concentrations (Ferreira et al., 2003): i) spontaneous precipitation of hydroxyapatite (HAP); ii) complete dissolution of calcium and HAP growth; iii) appearance of first nuclei of brushite; iv) coexistence of HAP and brushite and v) transformation of HAP into brushite and growth of brushite. The last stage represents the main challenge with respect to the precipitation rate modelling because it has to take simultaneously into account two kinetics phenomena: brushite grows first, due to direct consumption of calcium in the solution and second, due to the transformation of HAP into brushite.

The dynamical model of this last stage, transformation of HAP into brushite and growth of brushite, according to the general formulation (3) is

$$\frac{dM_c}{dt} = -q_{m1}\varphi(M_c, M_{HAP}, M_B) \quad (17)$$

$$\frac{dM_{HAP}}{dt} = -K_{HAP}(M_{HAP})^2 \quad (18)$$

$$\frac{dM_B}{dt} = \varphi + 10q_{m2}K_{HAP}(M_{HAP})^2, \quad (19)$$

where M_c is the mass of calcium into solution, M_{HAP} is the mass of HAP and M_B is the mass of brushite. $\varphi(\cdot)$ is the precipitation rate, q_{m1}, q_{m2} are molar weight ratios.

Since M_{HAP} does not depend on φ and only two states explicitly depend on the reaction rate, one of which is measured (M_c), we can simplify the general algorithm presented in section III and choose equal state partitions (6) and (9) as follows

$$X_a = X_1 = M_c, \quad X_b = X_2 = M_B, \quad (20)$$

with

$$K_a = -q_{m1}, \quad K_b = 1 \quad (21)$$

$$A_0 = A_1 = 1/q_{m1} \quad A_2 = 1. \quad (22)$$

According to (10), the state observer required to recover M_B is the following

$$\frac{d\hat{M}_{HAP}}{dt} = -K_{HAP}(M_{HAP})^2 \quad (23.1)$$

$$\frac{d\hat{Z}}{dt} = 10q_{m2}K_{HAP}(\hat{M}_{HAP})^2, \quad (23.2)$$

$$\hat{M}_B = \hat{Z} - \frac{1}{q_{m1}}M_c. \quad (23.3)$$

The observation error is

$$E_x = \begin{bmatrix} M_c - \hat{M}_c \\ M_B - \hat{M}_B \end{bmatrix}, \quad (24)$$

with respective matrices

$$D=0, \quad \Omega = \begin{bmatrix} -\omega_1 & 0 \\ 0 & -\omega_2 \end{bmatrix}. \quad (25)$$

For the current study, the value of $\omega_1 = \omega_2 = 0.5$ was chosen after trial and error. Finally, the NN error is

$$E_\varphi = \frac{1}{q_{m1}} \begin{bmatrix} \left(\dot{M}_c - \hat{M}_c \right) - \omega_1 (M_c - \hat{M}_c) \\ \left(\dot{M}_B - \hat{M}_B \right) - \omega_2 (M_B - \hat{M}_B) \end{bmatrix}. \quad (26)$$

For the numerical realization, the error at each iteration is determined as follows

$$E_{\varphi(i)} = \frac{1}{q_{m1}} \left[\frac{M_{c(i)} - M_{c(i-1)}}{T} - \frac{\hat{M}_{c(i)} - \hat{M}_{c(i-1)}}{T} - \omega_1 (M_{c(i)} - \hat{M}_{c(i)}) \right] + \left[\frac{M_{B(i)} - M_{B(i-1)}}{T} - \frac{\hat{M}_{B(i)} - \hat{M}_{B(i-1)}}{T} - \omega_2 (M_{B(i)} - \hat{M}_{B(i)}) \right] \quad (27)$$

A feedforward NN with 2 inputs (M_c, M_B), 1 output (φ_{NN}), one hidden layer with 7 sigmoid nodes was trained to minimise the error (27). The Marquardt backpropagation training algorithm was preferred since the authors have successful experience with this algorithm in a number of NN regression and control applications.

V. RESULTS

The KBHM model is evaluated for its ability to predict process behavior for various initial concentrations of reagents (0.05, 0.1, 0.2, 0.3, and 0.4 M). The results are summarized in Fig. 3 and Fig. 4. Data for the main system states (M_c - measured, M_{HAP} and M_B - estimated) are denoted by dashed line in all figures on subplots a), c) and d), respectively. Data for average particle size (AM) is

denoted by stars in all subplots b). The model time trajectories of M_c (subplots a) and AM (subplots b)) are direct indicators of the model quality since measurements for them are available. The mass of HAP and brushite are not directly measured variables but they can be inferred by the available measurements. Thus, the plots of M_{HAP} (subplots c) and M_B (subplots d) are indirect indicators of the model reliability. Data from experiments with initial concentrations of reagents 0.2 and 0.3 M were used to train the NN, therefore it is not surprisingly that all model variables (M_c, M_{HAP}, M_B, AM) closely match the data from these two types of experiments (see Fig.3). However, more valuable are the results depicted in Fig. 4 where the model was tested on new ‘unseen’ validation data corresponding to experiments with different initial concentrations (0.05, 0.1 and 0.4 M). Data and model trajectories match quite well which confirms the ability of the hybrid NN to estimate the precipitation rate of calcium phosphate.

For the purpose of comparative analysis, three existing analytical models were also applied on the same task, see Table 1. The parameters of the fixed models were tuned with the same data obtained by experiments with (0.2 and 0.3 M) initial concentrations of reagents Here, we take the nondimensional error index (NDEI), which is defined as the root mean square error (RMSE) divided by the standard deviation of the target series.

VI. CONCLUSIONS AND DIRECTIONS FOR FURTHER RESEARCH

This paper presents the principles of a new NN supervised training procedure when target outputs are not available. The main contribution is related with the way how the error signal for updating the network weights is determined. The NN is connected with a partial fixed dynamical model to identify the process reaction rates. The proper selection of the fixed submodel and the estimation of its unmeasured states are also discussed.

Research, which is now going on, and will be reported soon as a continuation of this work, is to develop a strategy to estimate the reaction rates when the kinetics coefficients (the matrix K_{aug}) are not known. Several scenarios are considered as for example assuming all or not all of the process states are measured. The most challenging case is when both reaction rates and kinetics coefficients are to be estimated by data-based submodels. A number of possible solutions for the data-based modules are studied: classical ANN or fuzzy models, modular ANN, ect.

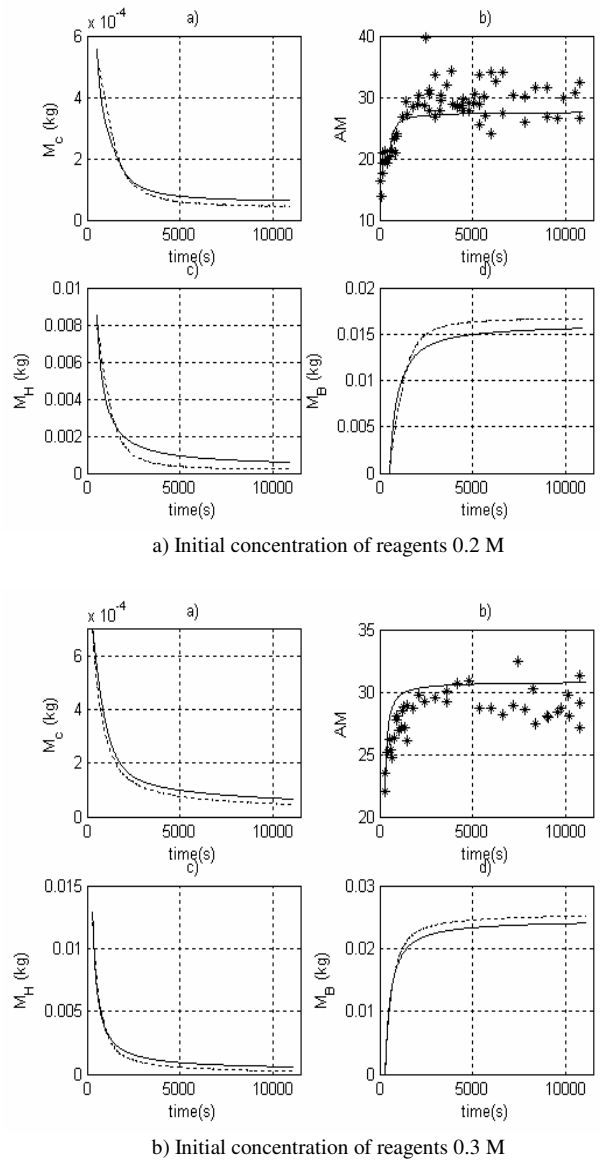
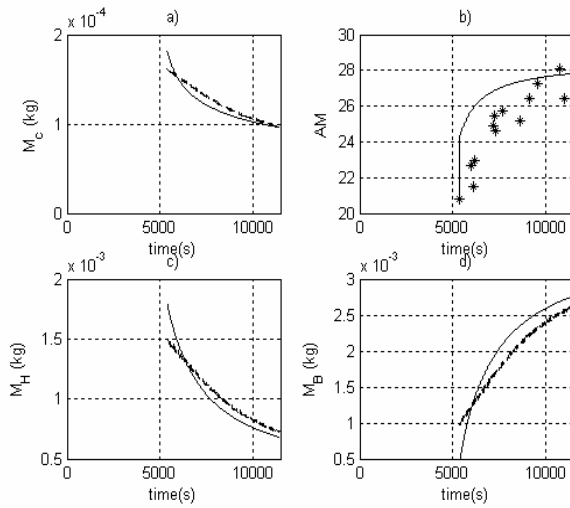
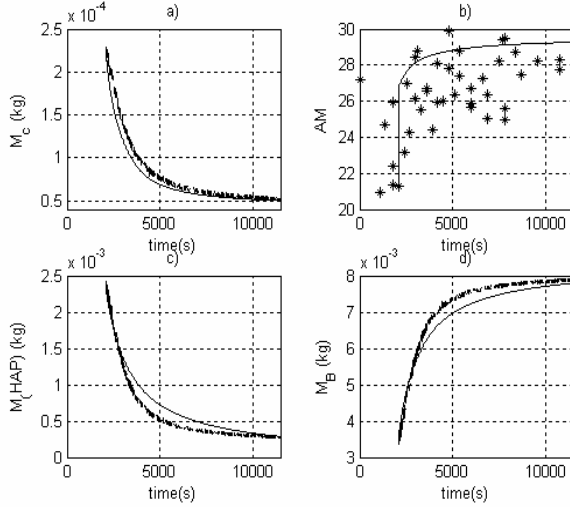


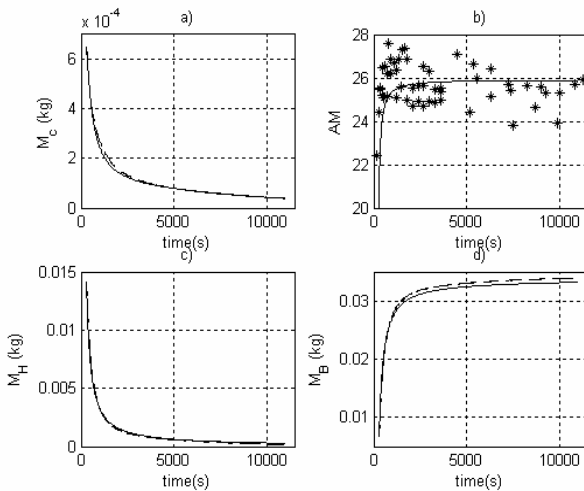
Fig.3 Results with the training data. Data points (dotted lines or stars) and the model estimations (solid lines) along time for a) Mass of calcium in solution, b) the average (in mass) particle size AM [μm]; c) Mass of HAP; d) Mass of brushite.



a) Initial concentration of reagents 0.05 M



b) Initial concentration of reagents 0.1 M



c) Initial concentration of reagents 0.4 M

Fig. 4 Results with the validation data. Data points (dashed line or stars) and the model estimations (solid lines) along time for a) Mass of calcium in solution, b) the average (in mass) particle size AM [μm]; c) Mass of HAP; d) Mass of brushite.

TABLE I ESTIMATION RESULTS FOR 3 ANALYTICAL MODELS AND THE KBHM

Calcium phosphate precipitation rate models	NDEI for model validation data
Monod type model (Lubenova et al., 2003) $\varphi = \frac{\lambda_{HAP1} M_{HAP}}{\beta_{HAP1} + M_{HAP}} + \frac{\lambda_{c1} M_c}{\beta_{c1} + M_c}$ $\lambda_{HAP1}, \lambda_{c1}, \beta_{HAP1}, \beta_{c1}$ - tuning parameters	0.404
Contois type model (Oliveira et al, 2002) $\varphi = \frac{\lambda_{HAP2} M_{HAP}}{\beta_{HAP2} M_B + M_{HAP}} + \frac{\lambda_{c2} M_c}{\beta_{c2} M_B + M_c}$ $\lambda_{HAP2}, \lambda_{c2}, \beta_{HAP2}, \beta_{c2}$ - tuning parameters	0.096
“Logistic” type model (Bastin and Dochain, 1990) $\varphi = \exp(-\lambda_3 M_B)$, λ_3 - tuning parameter	0.062
KBHM (this paper) A feedforward NN with 2 inputs (M_c , M_B), 1 output (φ_{NN}), one hidden layer with 7 sigmoid nodes	0.023

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