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Control of Bulk Propylene Polymerizations Operated with Multiple Catalysts through Controller Reconfiguration

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Abstract

This article presents a model to describe the dynamic behavior of bulk propylene polymerizations performed in a continuous reactor, assuming that three catalysts can be used. The model takes into account mass, energy and momentum balances, used to estimate the final polymer properties, including the melt index (MI) and extractables in xylene (XS). As the catalysts present different sensitivities to hydrogen, the proposed controller scheme considers that the MI control loop must be reconfigured in line and in real time when the catalysts are exchanged. Simulation results indicate that the reactor stability is maintained during specified production programs and that the desired final properties can be achieved satisfactorily. It is shown that control reconfiguration represents an alternative to overcome existing operation limits and recover operability when multiple catalysts are used at plant site.

Keywords – Control, polymerization, olefin, modeling, reconfiguration.

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1. Introduction

Polyolefins constitute very important classes of polymer materials, as these polymers find widespread use in many practical applications. For this reason, there is strong economic interest in polyolefin materials, explaining the multibillion polyolefin market worldwide and the production of 140 million tons of polypropylenes (PP) and polyethylenes (PE) in 2008 (Moore and Larson, 1996; Chum and Swogger, 2008). Particularly, the PP market grows at annual rates that are close to 10%, showing the increasing importance of polyolefin materials in the modern world (Zhang *et al.*, 2010). Given the importance of the polyolefin business, academic and industrial investigations have been performed continuously to improve the general understanding of olefin polymerization reactions and processes.

In the particular case of PP reactions, different types of polymerization processes have already been proposed, although usual commercial processes are heterogeneous and performed in suspensions of liquid monomer, in tank or tubular reactors (Mattos Neto and Pinto, 2001).

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1 Depending on the desired final PP properties, catalysts with different properties can be used
2 (Kiparissides, 1996; Cho *et al.*, 2000).
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4 A fundamental problem of polymerization technologies is the determination of the proper
5 operation policies required to achieve and control the desired quality and production rates of
6 the final polymer material. However, accomplishment of this important task can be very
7 difficult, because most polymerization processes are designed to produce resins with different
8 final properties and meet different market demands. This operation flexibility can be reached
9 through different ways: (1) using multiple reactors, which can be operated at different
10 conditions (including temperatures, pressures and hydrogen partial pressures, manipulated to
11 control the average sizes of polymer chains and the chain size distribution); (2) using different
12 catalysts and catalyst mixtures; (3) combining the two previous alternatives (Cho *et al.*, 2000).
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15 Although the use of multiple reaction vessels in industrial polymerization sites is common,
16 constituting a mature technological alternative for increase of process flexibility, fixed
17 investment costs required by these processes can be very high. On the other hand, the use of
18 multiple catalysts and catalyst mixtures at plant site is not very common, although this can
19 constitute an appealing alternative for increase of process flexibility with relatively low
20 impact on the process economics. However, analyses of control issues related to use of
21 different catalysts in the same plant, when these catalysts present different sensitivities to
22 changes of the process operation conditions, are still missing. Generally, the catalyst and the
23 polymerization process are regarded as two parts of a single integrated technological system,
24 with little room for modification of one part without changing the other one.
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27 Several types of catalysts have already been proposed for production of PP resins. From a
28 commercial perspective, Ziegler-Natta (ZN) catalysts still constitute the most important class
29 of catalysts. Despite that, other catalysts are being introduced slowly into the PP business,
30 such as the metallocene catalysts (MC), because of the distinct properties of the final
31 produced resins, including the narrower molecular weight distributions and the peculiar
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1 stereochemical properties of the macromolecular chains (Marques *et al.*, 1998). For this
2 reason, there are incentives to use multiple catalysts at a single production site.
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4 From a practical point of view, the most important differences between commercial ZN and
5 MC catalysts (or other different catalysts in a mixture) are the catalyst activity, sensitivity to
6 hydrogen, degree of isotacticity of the produced polymer and sensitivity to reaction
7 temperatures. These differences can be particularly important for process operation, as
8 catalyst feed flow rates, reaction temperatures and hydrogen feed flow rates are normally
9 manipulated to control the molecular weight averages and the rates of polymer production at
10 plant site. As a consequence, important operational limitations can be faced by the engineer
11 when catalysts with different characteristics are used in a single plant site. In this case, in
12 order to maintain the process operability and safety, it may be necessary to develop and
13 implement advanced operational strategies to mix or exchange the different manipulated
14 catalysts in the process.
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31 As the reaction kinetics of different catalyst systems can be quite different, it is of paramount
32 importance to comprehend how process variables affect the catalyst performance in each
33 particular case. Depending on the catalyst, as the process outputs may respond differently to
34 modification of the manipulated process variables, the control configuration should not be
35 necessarily unique.
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43 More specifically, the control of the melt index (MI) of PP resins produced with ZN catalysts
44 is normally performed through manipulation of the hydrogen feed flow rate (Ali *et al.*, 2006),
45 as hydrogen is a well-known chain transfer agent (CTA) for this system. However, many MC
46 catalysts do not respond effectively to variations of hydrogen concentrations, forcing the use
47 of other process variables in order to keep the MI (and other properties) under control. For
48 example, the rate of spontaneous chain transfer through β -scission can be manipulated by
49 means of modification of the reactor temperature, allowing for control of the MI.
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1 activity and rates of polymer production, so that the performance of the control loop depends
2 on the analyzed catalyst or mixture of catalysts, which implies that the control scheme must
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4 be reconfigured for each particular operation condition.
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7 Assuring the operability of chemical processes within predetermined operational limits
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9 constitutes one of the key factors that have motivated modern research in the process control
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11 field (Srinivasan and Qian, 2006). However, assuring process operability can constitute a
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13 difficult task when traditional control schemes are used, as traditional controllers do not
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15 present the ability to adapt the control procedures during the occurrence of transients and
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17 abnormal events at the plant. In order to adapt the controller performance to the plant
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19 operation, some approaches propose the use of adaptive strategies, including the
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21 decomposition of the process operation into modes, the design of fault tolerant control
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23 schemes, the use of model based controllers, implementation of advanced process monitoring
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25 techniques and use of system reconfiguration tools (Åström and Wittenmark, 1997; Rodriguez
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27 *et al.*, 2003; Steffen, 2005; Zhang and Jiang, 2008; Rawlings and Mayne, 2009).
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34 Among these different alternatives, control system reconfiguration can constitute a useful tool
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36 to enable the transition between different regions of the operating space, involving the
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38 modification of the internal structure and/or tuning parameters of the controller in order to
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40 meet the required performance indexes of the process operation (Benítez-Pérez *et al.*, 2007).
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42 In this case, the main pursued objectives should be meeting the product specifications
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44 (product quality) along an optimum trajectory, while keeping the stability and safety of the
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46 process operation (Tran *et al.*, 2007). A reconfiguration scheme has been proposed recently
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48 for a gas phase polyethylene reactor in order to detect faulty actuators and guarantee the safe
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50 operation of the polymerization process (Gani *et al.*, 2007). A model migration method has
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52 also been proposed to perform the on-line adaptation of a soft-sensor model used to control a
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54 polyvinyl chloride (PVC) polymerization process (Wang and Guo, 2013).
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1 State (grade) transitions have received a lot of attention in the literature regarding
2 polymerization reaction systems, as many industrial plants produce tens of different polymer
3 materials (polymer grades) in order to meet the expectations of distinct clients. For this
4 reason, optimization of grade transition trajectories is of fundamental importance for
5 improvement of product quality and maximization of economic benefits (Benamor *et al.*,
6 2004; Prata *et al.*, 2008). Generally, grade transition studies focus on the implementation of
7 stable, safe and fault-free operation trajectories intended to minimize the transition period,
8 prevent off-spec production and avoid plant shutdown (Srinivasan *et al.*, 2005). To date, no
9 controller reconfiguration scheme has been proposed in order to extend the plant operation to
10 the entire range of product specifications when multiple catalysts are used at plant site.
11

12 Based on the previous paragraphs, the present work analyzes the control of a continuous
13 propylene bulk polymerization process, when three distinct catalysts are used at plant site to
14 produce polymer grades with distinct final properties. In order to do that, an advanced control
15 scheme is proposed to allow for catalyst exchange and simultaneously keep product
16 specification under control during grade change. The proposed scheme assumes that a
17 production program is available, defining the required product properties, the catalyst to be
18 used and the sizes of the lots (in other words, the duration of the campaigns). In order to
19 perform the scheduled production program, the control system must introduce the necessary
20 changes in the supervisory layer (updating set-points and reconfiguring the control loops),
21 while the regulatory layer must be able to keep track of the pre-defined set-points. As shown
22 in the following sections, this proposed control approach allows for proper control of the
23 process operation even when the used catalysts present very different kinetic characteristics,
24 leading to products with the desired properties and simultaneously keeping the process
25 operation stable.
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2. Polymerization Process

Process model

The process studied here is the bulk PP polymerization process (LIPP, liquid pool polymerization technology) performed in a stirred tank reactor (300 m³), as described by Prata *et al.* (2009). The simplified flow chart for this polymerization process is shown in **Figure 1**.

As the polymerization reaction is very exothermic, top condensers are used to remove the reaction heat. The monomer is fed into the reactor in the liquid phase, as the process is operated at 30 atm. Catalysts and other reagents are also fed into the reactor through the monomer liquid stream. The reactor outlet stream is composed mainly of unreacted propylene and polypropylene. PP (and other solid species) is separated from propylene through reduction of operating pressure, while the remaining volatile chemical species are recycled. Prata *et al.* (2009) presented a detailed description of the real industrial process, developed and implemented a process model for reconciliation of dynamic data and validated the model with operation data in real time. For this reason, the interested reader is encouraged to consult the original reference for additional process details.

[Figure 1]

The present work assumes that three distinct catalysts must be used at plant site, while the original work considered the existence of a single catalyst in the feed stream. **Table 1** specifies the relevant catalyst properties considered here for simulation and summarizes the main characteristics of the obtained polymers. The catalyst properties assume that two ZN catalysts and one MC catalyst can be used at plant site. Although distinct catalyst systems can require the use of distinct cocatalysts and electron donors, it is also assumed here that triethylaluminium (TEA) can represent the mixture of cocatalysts, that para-ethoxy ethyl benzoate (PEEB) can represent the mixture of external electron donors and that hydrogen is used as the CTA. The simplified kinetic mechanism for each analyzed catalyst is presented in **Table 2**.

[Table 1]

[Table 2]

Based on information presented in Figure 1 and Tables 1 and 2, the mathematical model that describes the bulk PP polymerization process can be written as (Prata *et al.*, 2009):

Global mass balance

$$\rho \frac{dV}{dt} = \dot{m}_M + \dot{m}_H + \dot{m}_{TEA} + \dot{m}_{PEEB} - \dot{m}_S \quad (1)$$

Monomer mass balance

$$\frac{d(V \cdot M)}{dt} = \frac{\dot{m}_M - w_M \dot{m}_S}{PM_M} - VM \sum_j (k_{p,j} + k_{tm,j}) Cat_j \quad (2)$$

Catalyst mass balance

$$\frac{d(V \cdot Cat_j)}{dt} = \dot{m}_{Cat,j} - \left(\frac{\dot{m}_S}{\rho} \right) Cat_j - V k_{d,j} Cat_j \quad (3)$$

Hydrogen mass balance

$$\frac{d(V \cdot H_2)}{dt} = \frac{\dot{m}_H}{PM_H} - \left(\frac{\dot{m}_S}{\rho} \right) H_2 - V H_2 \sum_j k_{th,j} Cat_j \quad (4)$$

Polymer mass balance

$$\frac{dPol}{dt} = R_{Pol} - \dot{m}_{pol} \quad (5)$$

Cocatalyst mass balance

$$\frac{dTEA}{dt} = \dot{m}_{TEA} - \left(\frac{TEA}{Pol} \right) \dot{m}_{pol} \quad (6)$$

Electron donor mass balance

$$\frac{dPEEB}{dt} = \dot{m}_{PEEB} - \left(\frac{PEEB}{Pol} \right) \dot{m}_{pol} \quad (7)$$

Reaction rate

$$R_{Pol} = -PM_M \cdot V \cdot M \sum_j k_{p,j} Cat_j \quad (8)$$

Polymer separation

$$\dot{m}_{pol} = \dot{m}_S - \dot{m}_{gas} \quad (9)$$

Composition constraint

$$\dot{m}_{gas} = (1 - w_M) \dot{m}_S \quad (10)$$

Density

$$\rho = w_M \rho_M + w_{pol} \rho_{pol} \quad (11)$$

Momentum balances of living polymer chains

$$\frac{d\lambda_{0,j}}{dt} = \frac{dCat_j}{dt} \quad (12)$$

$$\frac{d(V \cdot \lambda_{1,j})}{dt} = - \left(\frac{\dot{m}_S}{\rho} \right) \lambda_{1,j} + V \left[k_{p,j} M Cat_j - (k_{tH,j} H_2 + k_{ts,j} + k_{d,j}) \lambda_{1,j} \right] \quad (13)$$

$$\frac{d(V \cdot \lambda_{2,j})}{dt} = - \left(\frac{\dot{m}_S}{\rho} \right) \lambda_{2,j} + V \left[k_{p,j} M (Cat_j + 2\lambda_{1,j}) - (k_{tH,j} H_2 + k_{ts,j} + k_{d,j}) \lambda_{2,j} \right] \quad (14)$$

Momentum balances of dead polymer chains

$$\frac{d(V \cdot \mu_{k,j})}{dt} = - \left(\frac{\dot{m}_S}{\rho} \right) \mu_{k,j} + (k_{tH,j} H_2 + k_{ts,j} + k_{d,j}) \lambda_{k,j} V \quad (15)$$

Energy balance in the reactor

$$\frac{dT}{dt} = \frac{\dot{m}_M c_{p,M}(T_e) \cdot (T_e - T) + (-\Delta H) R_{pol} - Q_1}{PM_M c_{p,M}(T) VM + c_{p,Pol}(T) Pol} \quad (16)$$

Energy balance in the condenser

$$\frac{dT_c}{dt} = \frac{Q_1 - Q_2}{M_c \cdot c_{p,M}(T_c)} \quad (17)$$

Energy balance in the jacket

$$\frac{dT_w}{dt} = \frac{\dot{m}_w c_{p,w}(T_{we}) \cdot (T_{we} - T_w) + Q_2}{M_{cw} \cdot c_{p,w}(T_w)} \quad (18)$$

Heat exchanged through the condenser

$$Q_1 = \dot{m}_{M_c} \left[c_{p,M}(T) \cdot (T - T_c) + \lambda_M(T) \right] \quad (19)$$

Heat exchanged through the jacket

$$Q_2 = UA(T_c - T_w) \quad (20)$$

Physical properties, as density, heat capacity and heat of vaporization, are known functions of the reactor temperature, as given by Equation 21 to 27 (Wilkinson and Dole, 1962; Mattos Neto and Pinto., 2000).

Monomer density

$$\rho_M(T) = -1.0878 \cdot 10^{-5} T^2 + 4.7376 \cdot 10^{-3} T + 6.0983 \cdot 10^{-2} \quad (21)$$

Polymer density

$$\rho_{Pol}(T) = -2.0888 \cdot 10^{-6} T^2 + 9.5767 \cdot 10^{-4} T + 8.0950 \cdot 10^{-1} \quad (22)$$

Specific heat capacity of monomer

$$c_{p,M}(T) = 1.98685 \cdot 10^{-3} \cdot \delta(T)^{-2} + 0.646454 - 0.846918 \cdot \delta(T) + 1.3177 \cdot \delta(T)^2 - 3.00842 \cdot \delta(T)^3 + 14.04220 \cdot \delta(T)^4 - 17.4783 \cdot \delta(T)^5 \quad (23)$$

Specific heat capacity of polymer

$$c_{p,pol}(T) = 0.3669 + 0.00242(T - 273.15) \quad (24)$$

Specific heat capacity of water

$$c_{p,w}(T) = 3.6653 - 2.77195 \cdot 10^{-2} T_w + 1.07756 \cdot 10^{-4} T_w^2 - 1.87210 \cdot 10^{-7} T_w^3 - 1.24269 \cdot 10^{-10} T_w^4 \quad (25)$$

Latent heat of vaporization of monomer

$$\lambda_M(T) = \frac{2.6380 \cdot 10^7}{4.1855 \cdot PM_M} \delta(T)^{0.37261} \quad (26)$$

$$\delta(T) = 1 - \frac{T}{364.9} \quad (27)$$

Different properties are normally used to characterize the final quality of the obtained polymer material, including the molecular weight averages, polydispersity, melt index, xylene extractable fraction (XS), among others. XS indicates the total amount of atactic and oligomer fractions in the resin and can be related to the stiffness of the final material (Latado *et al.*, 2001; Machado and Pinto, 2011). The weight-average molecular weight (M_w), the number-average molecular weight (M_n) and the polydispersity index (PD) can be obtained from the momentum balances of the polymer chains (Mattos Neto *et al.*, 2005). Based on the averages, and remaining compositions, the MI (Latado *et al.*, 2001) and the XS (Machado and Pinto, 2011) can also be calculated, as shown in Equation 28 to 32.

Weight-average molecular weight

$$M_w = PM_M \frac{\sum_{j=1}^3 (\lambda_{2,j} + \mu_{2,j})}{\sum_{j=1}^3 (\lambda_{1,j} + \mu_{1,j})} \quad (28)$$

Number-average molecular weight

$$M_n = PM_M \frac{\sum_{j=1}^3 (\lambda_{1,j} + \mu_{1,j})}{\sum_{j=1}^3 (\lambda_{0,j} + \mu_{0,j})} \quad (29)$$

Polydispersity

$$PD = M_w / M_n \quad (30)$$

MI

$$\log(MI) = a_1 \log(M_w) + a_2 \quad (31)$$

XS

$$\frac{dXS}{dt} = \frac{R_p}{Pol} \left[XS^R + K_{XS} \cdot \left(\frac{TEA}{PEEB} - 1 \right) - XS \right] \quad (32)$$

Numerical Implementation

The mathematical model was implemented in Matlab to perform the simulations, using the routine ode15s.m for numerical integration, which is suitable for dynamic simulations of stiff systems (Shamiri *et al.*, 2010). The kinetic constants were implemented in the form of the Equation 33, where activation energy values are presented in **Table 3**.

$$k(T) = k_0 \cdot \exp \left[- \left(\frac{E}{R} \right) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (33)$$

Activation energies were assumed to be the same for the three catalysts, although this simplification does not lead to any modification of the significance of obtained simulation results, as observed through many simulation tests. Although it is true that modification of activation energies leads to different temperature trajectories, temperature changes are driven mainly by the distinct catalyst sensitivities to modification of process variables. Remaining process and catalyst parameters required for simulation are presented in **Table 4** and **5**. It must be noted that the parameters required for calculation of XS are different for different catalysts, indicating that each catalyst presents different sensitivities to modification of concentrations (compositions) of cocatalysts and electron donors. In order to keep the process operation within feasible values, the set of process constrains presented in **Table 6** was also implemented to account for inadequate control action and to represent the existence of real operational limits.

[Table 3]

[Table 4]

[Table 5]

[Table 6]

3. Control configuration

The proposed control system comprises two hierarchical layers, which are separated by the time scale needed to take the control actions. The lower control layer (regulatory) is responsible to keep the process operation at the desired point, by keeping key variables around nominal conditions. The regulatory control must be performed more often than the upper layer (supervisory) control in order to mitigate disturbance effects on the process stability. For this reason, it is assumed here that the characteristic sampling times of regulatory and supervisory layers are equal to 1 and 10 min respectively, according with sampling times practiced in real plants (Congalidis and Richards, 2006). Therefore, upper layer control actions are carried out ten times less frequently than lower layer control actions.

The regulatory layer comprises the control of reactor temperature, condenser temperature and reactor volume through manipulation of condensate rate from the condenser, coolant feed rate to the condenser and slurry flow rate from the reactor. Additionally, the process productivity, defined as the ratio between output polymer flow rates and monomer feed rates ($\dot{m}_{pol} / \dot{m}_M$), is also controlled through manipulation of the catalyst feed rate. Control of process productivity is of fundamental importance for the process economics.

The supervisory control layer is related to control of the final quality of the produced polymer material (XS and MI). In order to control the XS, the ratio $\dot{m}_{TEA} / \dot{m}_{PEEB}$ is manipulated at plant site. In order to control the MI, the control configuration depends on the particular employed catalyst. The hydrogen feed rate must be manipulated to control the MI when ZN catalysts are employed. On the other hand, in the case of the MC catalyst, the reactor temperature must be manipulated to control the MI, as this is the only remaining degree of freedom available to affect the MI. Based on this topology, the MI control loop constitutes the primary control loop

1 in a cascade control arrangement for control of the reactor temperature. In the industrial
2 practice, changes of the reactor temperature are usually undesired for safety reasons and
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4 because temperature changes lead to modification of catalyst activity and possible
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6 modification of the catalyst structure. For this reason, process operation is normally
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8 performed around a constant reactor temperature set-point.
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11 The proposed control structures can be seen in **Figures 2-a** and **2-b** for the ZN and MC
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13 catalysts respectively. The PI controllers were implemented according to the discrete velocity
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15 algorithm given by Equation 34. The parameters used to perform the PI control are shown in
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17 **Table 7**. In order to avoid sudden changes of manipulated variables between sampling times,
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19 the relative variations of manipulated variables were constrained to specified limits. The
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21 control parameters were defined by simulation, through observation of the state variable
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23 responses to modifications of the input variables (the initial guesses were obtained through
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25 standard Ziegler-Nichols tuning around pre-defined steady states).
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31 [Figure 2-a]

32 [Figure 2-b]

33 [Table 7]

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$$u(t_k) = u(t_{k-1}) + K_C \left(e(t_k) - e(t_{k-1}) + T_s \frac{e(t_k)}{\tau_I} \right) \quad (34)$$

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47 Preliminary tests

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49 The initial tests considered the tracking of the nominal polymer specifications (**Table 8**) using
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51 a single catalyst, in order to check the opportunities and limitations of each particular form of
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53 polymer production. The obtained responses can be seen below. In general, the operation is
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55 stable with all catalysts, even when the specifications are very different from their nominal
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57 values. The manipulation of the input variables was always smooth and the use of the same PI
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controllers showed that the implemented parameters ensured sufficient robustness to the analyzed control structures.

[Table 8]

The operation with the ZN catalysts is very versatile to meet the desired product specifications. It is worth noting that a lower amount of Cat₁ is needed to maintain the productivity control, as can be seen in **Figures 3-a** and **3-b**. However, this catalyst requires higher hydrogen feed rates to keep the control of the melting index (**Figures 3-c** and **3-d**). This is because the relationship between the kinetic constants for propagation and chain transfer to hydrogen is higher for Cat₁, that is, $k_{p,1}/k_{tH,1} = 15$ e $k_{p,2}/k_{tH,2} = 6.67$ at the defined operating temperature.

[Figure 3-a]

[Figure 3-b]

[Figure 3-c]

[Figure 3-d]

When working with Cat₃, productivity is slightly affected by the manipulation of reactor temperature. However, manipulation of the catalyst feed rate suffices to ensure the maintenance of the productivity. The melting index responses show that higher MI values require the operation at higher temperatures, so that the reactor is forced to operate near its maximum temperature limit. When the specification of $20 \text{ g (10 min)}^{-1}$ is imposed to the polymer MI, an important limitation arises, as shown in **Figure 3-e**, since the reactor temperature reaches its maximum limit ($T_{\max} \leq 360 \text{ K}$). At this point, the temperature constraint constitutes an operating limit for Cat₃ and the maximum achievable value for the MI is $12.35 \text{ g (10 min)}^{-1}$. As a result, the inability to produce polymers with higher MI values may impose the need for catalyst exchange at plant site. In this case, the reconfiguration of the melting index control loop must be performed accordingly.

[Figure 3-e]

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Regarding the XS, **Figure 3-f** shows that the control is adequate when the specification coincides with the nominal operation values of the employed catalysts, leading to $\dot{m}_{TEA} / \dot{m}_{PEEB}$ ratios close to one (**Figure 3-g**). Among the catalysts, the operation with Cat₃ is the one that exhibits faster transitions, leading to production of lower amounts of *off-spec* material. However, significant offsets can also be observed due to limitations of the catalyst performances. Process limitations become clear when one specifies XS values of 0.5 %wt/wt for the final resin, for example. In this case, operation with Cat₁ and Cat₂ lead to XS values of 0.85 and 1.30 %wt/wt, respectively, and significant offsets. According to the XS steady-state balance, in both cases it would be necessary to operate with negative ratios TEA/PEEB, which is obviously not feasible and explain the observed offsets. Therefore, replacement of both Cat₁ and Cat₂ by Cat₃ would be necessary at plant site in order to reach the desired low XS values. This shows that each catalyst can provide XS values within well defined ranges, due to its inherent kinetic properties, which may impose the need to exchange the catalysts at plant site.

[Figure 3-f]

[Figure 3-g]

Based on these preliminary results, one can highlight some practical issues and propose some guidelines regarding the application of the analyzed catalysts, as described in **Table 9**. An important partial conclusion that can be presented at this point is that different catalysts must be used to produce different polymer products. For example, when the objective is to produce a polymer with low XS and MI values, it is interesting to work with Cat₃; in the case of high MI, both Cat₁ and Cat₂ can be used; when it is needed to reduce the consumption of hydrogen, while maintaining the high MI values, the use of Cat₂ is preferable. Thus, when it is necessary to run the process in a broad space of operation conditions, it may be interesting to use different catalysts and devise operation strategies to perform catalyst exchanges at plant site.

[Table 9]

Proposed catalyst exchange scheme

In order to analyze the control performance, it is assumed first that the operation is always performed with a single catalyst in the monomer feed, although catalyst exchange can be performed at plant site. Besides the reasons presented in the previous section, there may be additional motivation to perform catalyst exchange at plant site, including problems with catalyst decay, when the operation temperature and residence time change, and with low sensitivity to changes of the feed hydrogen concentration.

The proposed scheme for catalyst exchange involves reconfiguration of the MI control loop. As the underlying kinetic mechanisms of the analyzed catalysts are different, two operation strategies are proposed, according to the behavior imposed on the process variables and in order to guarantee the stability of the reactor temperature control.

Strategy A

When it is desired to employ the MC, Cat_3 , in a new campaign, one might suggest feeding Cat_3 only after reaching the new MI specification value, using the catalyst from the previous campaign (Cat_1 or Cat_2). As the MI control must be performed through manipulation of the reactor temperature for Cat_3 , one might face problems with the energy balance of the process in this case. For this reason, it is assumed that feeding of Cat_3 can be initiated as soon as the new campaign is started. In order to initiate the feeding of Cat_3 smoothly, the productivity control is performed through manipulation of the Cat_3 feed rate, while hydrogen and the previous catalyst feed rates are reduced with the help of a first-order filter. The sharp reduction of hydrogen feed rates should be avoided because the remaining Cat_1 or Cat_2 inside the reactor would cause the production of polymer material with very low MI. In the beginning of the catalyst exchange operation, as the hydrogen concentration is reduced and the MC concentration increases inside the reactor, the MI is expected to decrease, leading to production of *off-spec* material. In fact, an ideal operation strategy should drive the process

1 directly to the desired operating temperature of the new campaign with Cat₃, although this
2 may be difficult to define *a priori* because the optimum temperature trajectory depends on the
3
4 initial process states when the catalyst transition is started and on the desired final polymer
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6 properties.
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10 **Strategy B**

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12 When it is desired to exchange the MC, Cat₃, for the ZN, Cat₁ or Cat₂, definition of the
13
14 operation procedure poses some challenges. One may be tempted to drive the reactor
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16 temperature directly to the nominal operating temperature of the ZN catalysts, but this may
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18 cause serious problems to the MI control and production of large amounts of *off-spec*
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20 material. In order to overcome this problem, one may follow the same ideas presented earlier
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22 and initiate feeding of the new catalyst in the beginning of the new campaign, allowing for the
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24 control system to keep the output variables under control, with the continuous and smooth
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26 modification of the reactor temperature.
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33 In this case, the MI control loop must be reconfigured to allow for manipulation of the
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35 hydrogen feed rate. However, in order to avoid sudden changes and significant production of
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37 *off-spec* material, hydrogen feeding must be initiated before triggering of the reactor control
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39 reconfiguration. **Figure 4** illustrates this particular point, for a window of 30 h of production.
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43 In this case, there is a melting index grade change from 7.5 to 15 g (10 min)⁻¹ starting at the
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45 instant of 10 h. One must observe in **Figure 4** that initiating the hydrogen feed only after
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47 reconfiguration of the MI control loop leads to production of *off-spec* material for about 4 h.
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51 However, as the catalyst exchange is a scheduled task (i.e., the moment when exchange takes
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53 place is known), the proposed solution is ensuring that the reaction mixture has a sufficient
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55 quantity of hydrogen when catalyst Cat₁ or Cat₂ is fed. For example, one can assume that the
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57 control structure reconfiguration can only be triggered when the molar concentration of
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59 hydrogen (or total amount of hydrogen fed into the reactor) reaches a minimum limit value
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1 (for instance, 0.01 mol l⁻¹). In order to complete the control strategy, the productivity control
2 should be performed with the new campaign catalyst, while the feed rate of Cat₃ should be
3 reduced with the help of a first-order filter.
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6
7 [Figure 4]
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9 **Figure 5** illustrates the two proposed strategies for control reconfiguration. Both strategies
10 were implemented in order to perform automatically a production list, which must inform the
11 final desired polymer properties and the moments when the necessary process changes must
12 be implemented. The production list is presented as a timeline of required specifications (SP_n)
13 for a given catalyst available or regarded as appropriate (Cat_{j,n}, where j = 1, 2, 3), as shown in
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21 **Table 10.**
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24 [Figure 5]
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26 [Table 10]
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29 When a list is available, a preliminary verification step is performed to check if the current
30 catalyst matches to the desired one. If the answer is positive, the campaign is continued up to
31 the next sampling time of the supervisory control layer. However, the change of some
32 operational and polymer specifications can be performed if desired. If the catalyst does not
33 match the production list, then the guidelines outlined before for strategies A and B must be
34 taken in order to implement the correct catalyst exchange procedures for the new campaign,
35 as illustrated in **Figure 6**.
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46 [Figure 6]
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49 **Catalyst exchange tests**

50 In this second test section, four operating scenarios were assumed, including grade and
51 production rate changes. The catalyst exchange was simulated as indicated by a production
52 list designed to produce polymer materials with defined specifications. It is always assumed
53 that the desired resin properties were sent to the supervisory control layer after 10 hours of
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1 operation and were implemented with the help of a first-order filter, given by Equation 35
2 (also used to perform feed rate exchanges). In this formulation, y_k^{set} represents the
3 implementation of the output set-points at sampling time k and y_{new}^{set} represents the new set-
4 points to be sent to the controllers. The parameter α is an adjustable parameter, made equal
5 to 0.95 in all simulations, unless stated otherwise.
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$$12 \quad y_k^{set} = \alpha \cdot y_{k-1}^{set} + (1 - \alpha) y_{new}^{set} \quad (35)$$

13 14 15 16 17 18 **Scenario 1: Cat₁ – Cat₃**

19 The motivation for this catalyst exchange operation is to maintain the production of
20 polypropylene with low MI, while reducing the XS. In order to implement the appropriate
21 control actions for this operating scenario, the strategy A should be considered, requiring the
22 MI control reconfiguration in order to manipulate the reactor temperature set-point. However,
23 the final value of this property should be kept constant at $7.5 \text{ g (10 min)}^{-1}$ from the prior
24 campaign, while XS is reduced from 3.0 to 0.5% wt/wt.
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35 It can be seen in **Figure 7-a** that the catalyst exchange was implemented at the time of
36 10 hours of operation with Cat₁, and that the time involved in the catalyst exchange procedure
37 was about 1 hour. As \dot{m}_{Cat_1} was reduced, the feed rate \dot{m}_{Cat_3} was increased, according to the
38 first-order filter and the continuous control of the productivity (**Figure 7-b**).
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45 [Figure 7-a]

46 [Figure 7-b]

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50 Regarding the XS response, **Figure 7-c** shows that the change in the desired value was
51 performed satisfactorily, reaching the desired final value in about 2 hours of operation and
52 with no steady-state offset. The manipulation of the cocatalyst feed rate ratio for this test is
53 given in the **Figure 7-d**.
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60 [Figure 7-c]

[Figure 7-d]

1
2 The melting index also showed an acceptable dynamic behavior (**Figure 7-e**). Actually, the
3 control of this property constitutes a regulatory problem, since its required value was constant.
4
5 It can be seen that significant deviations were observed in the first 3 hours of transition, with
6
7 maximum deviation from setpoint of 25%. The MI control was initially performed through
8
9 manipulation of the hydrogen feed rate and afterwards through manipulation of the reactor
10
11 temperature set-point (**Figures 7-f** and **7-g**). When the supervisory control system was
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13 notified, the hydrogen flow rate \dot{m}_H was continuously reduced and the reactor temperature
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15 was increased to about 350 K, so as to control Cat_3 activity and provide the desired MI value.
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22 [Figure 7-e]

23 [Figure 7-f]

24 [Figure 7-g]

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29 In order to observe the presence of other dynamic effects, it was also considered that the
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31 melting index was not constant in the production list, being necessary to produce a resin with
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33 MI of $5.0 \text{ g (10 min)}^{-1}$. In this case, the responses presented in **Figures 7-h** and **7-i** were
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35 obtained. Note that the MI control was also possible after the catalyst exchange and that the
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37 operating temperature was reduced by about 2 K.
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41 [Figure 7-h]

42 [Figure 7-i]

43 44 45 46 47 48 **Scenario 2: Cat_3 – Cat_2**

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51 In this example, it is required to increase the melting index beyond the feasible value given by
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53 Cat_3 and to keep constant the XS value, using low consumption of hydrogen. The control
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55 reconfiguration is to be implemented by means of strategy B, which indicates that the MI
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57 must be controlled through manipulation of the hydrogen feed rate. Specifically, the
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1 production list requires a grade change from 7.5 to 15 g (10 min)⁻¹ for MI, while the XS and
2 the reactor temperature are kept constant at 5.0% wt/wt and 348.4 K respectively.
3

4 In this case, the catalyst exchange was also possible and the productivity control response
5 showed a small deviation during the transition (**Figures 8-a** and **8-b**), which did not
6 compromise the performance. One must observe that the catalyst exchange took about 10 h,
7 because the filter parameter was set to 0.99 to prevent large initial deviations from desired
8 productivity and MI values. Particularly, the MI response presents a sudden and short
9 decrease when the catalyst exchange is started (**Figure 8-c**), although the controller tracks
10 tightly the desired trajectory as soon as the hydrogen feed rate is increased (**Figure 8-d**).
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21 [Figure 8-a]

22 [Figure 8-b]

23 [Figure 8-c]

24 [Figure 8-d]

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31 The proposed control strategy also allows for tight control of XS, as one can see in **Figure 8-**
32 **e**, although there is a maximum deviation from the desired value of about 6.7% wt/wt during
33 the transition time. After the catalyst exchange is finished, the manipulated ratio $\dot{m}_{TEA} / \dot{m}_{PEEB}$
34 is kept near one as expected (**Figure 8-f**), as the desired XS corresponds to the nominal
35 condition for catalyst Cat₂.
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43 [Figure 8-e]

44 [Figure 8-f]

45 46 47 48 49 50 51 **Scenario 3: Cat₃ – Cat₂ – Cat₁**

52 In this third example it is required to keep the MI constant and equal to 7.5 g (10 min)⁻¹, while
53 the XS values are allowed to vary along the three campaigns. Note that the first catalyst
54 exchange can be justified by the fact that a less expensive catalyst can be used to produce the
55 same polymer material. The second exchange is motivated by the fact that less amounts of
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1 catalyst can be used to produce the same polymer material. The exchange $Cat_3 - Cat_2$ must be
2 performed using strategy B for control reconfiguration; however, the second catalyst
3 exchange does not require any supervisory control reconfiguration.
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7 Catalyst exchanges for the three campaigns were implemented as shown in **Figure 9-a**.
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9 Polymer final properties responded as given in **Figures 9-b** and **9-c**. The MI response
10 exhibited important deviations from the desired values during the analyzed transitions,
11 especially when $Cat_2 - Cat_1$ exchange was implemented, as a consequence of the hydrogen
12 concentration problem. (This can be minimized if the hydrogen feed rate \dot{m}_H is increased,
13 although this is not pursued here.)
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21 [Figure 9-a]

22 [Figure 9-b]

23 [Figure 9-c]

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29 It can also be seen in **Figures 9-d** and **9-e** that control action variations are smooth (the initial
30 hydrogen feed rate peak is a control reconfiguration requirement, as already described).
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32 [Figure 9-d]

33 [Figure 9-e]

34 **Scenario 4: increasing propylene feed rate, + 25%**

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When it is needed to increase the polymer production, the only remaining degree of freedom
is the fresh monomer feed rate. In this example, it is assumed that the fresh monomer feed rate
 \dot{m}_M must be increased by 25% in order to meet the market demand. When the operation is
performed with catalyst Cat_1 , it is not possible to achieve high MI values (for instance,
 $20 \text{ g (10min)}^{-1}$), as the hydrogen feed rate constraint becomes active. For this reason, catalyst
exchange becomes necessary. The straightforward option is to operate with Cat_2 , since this
catalyst needs less hydrogen to maintain the same MI. Besides, the required MI cannot be

1 achieved with Cat₃. As one can see in **Figure 10-a**, in the first 10 hours \dot{m}_H was an active
2 constraint and there was a large offset on the MI control. However, after exchanging the
3 catalyst to Cat₂, proper MI control and increase of polymer production were attained
4 simultaneously. The initial overshoot of MI is related to the higher sensitivity of Cat₂ to
5 hydrogen. As shown in **Figure 10-b**, the hydrogen feed rate was decreased to about 1.75Kg h⁻¹
6 after catalyst exchange (**Figure 10-c**), which means that there is room for additional increase
7 of the polymer production and of the MI with Cat₂.
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16 [Figure 10-a]

17 [Figure 10-b]

18 [Figure 10-c]

19 Moreover, the control of XS is also satisfactory during the transition, as shown in **Figure 10-**
20 **d**, despite the overshoot that leads to maximum deviation of about 25% from the desired
21 reference, as a consequence of the larger XS nominal values of Cat₂, which requires
22 modification of the TEA/PEEB ratios.
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33 [Figure 10-d]

34 **Scheduling issues**

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38 Frequently, it is required to find an optimal sequence of production stages and transition
39 periods in order to obtain a specified amount of resin with specified quality. In this regard,
40 scheduling includes the determination of an optimal operation policy, designed to minimize
41 production of off-spec material and the transition time. In the analyzed polypropylene
42 process, scheduling must consider changes of monomer feed rates and composition, catalyst
43 exchange, modification of reaction temperature and changes of feed rates of hydrogen and
44 cocatalysts. All these operation variables constitute degrees of freedom for design of the
45 optimal operation conditions and stage sequence. In the particular case of the control
46 reconfiguration policy, one must also take into account the necessary structural changes
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1 required to keep the process operability and stability. However, it is important to highlight
2 that the scheduling task does not depend explicitly on the reconfiguration solution, as the
3 control layer is subjected to the designed production recipe and must take the control actions
4 needed to follow the scheduling instructions.
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9 As an example regarding how the scheduling task can be combined with the proposed
10 reconfiguration control scheme, a simple formulation for this grade transition problem
11 consider a given production sequence of polymer grades and the design of the catalyst
12 exchange time (t_{rec}) for minimization of the amount of off-spec product. Assuming that
13 deviations of 5% around the specified MI and XS targets are acceptable for the proposed
14 Scenario 1 (Cat₁ - Cat₃), it can be found that the optimum moment for initialization of the Cat₃
15 feed is placed two hours later than the original moment of the set point (grade) change
16 (Figure 11). The result is normalized in respect to the case when the Cat₃ feed is initiated
17 immediately after the set point change. It can be seen that the best solution leads to reduction
18 of almost 40% of the off-spec product. It can be inferred that Cat₁ can be partially used to
19 drive the operation up to the new specification point. Therefore, it is shown that the
20 scheduling task can be combined with control reconfiguration schemes for design of grade
21 transition trajectories and optimization of the process operation.
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41 [Figure 11]
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45 **Conclusion**

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47 This article analyzed the control of a bulk propylene polymerization process when multiple
48 catalysts are used to produce the final polymer resin. The use of multiple catalysts may be
49 necessary at plant site when it is required to increase the number of polymer grades or to
50 enlarge the range of properties of the produced polymer materials. The proposed control
51 scheme comprises two different layers: a regulatory layer (for control of reactor volume,
52 reactor temperature, polymer properties, among others) and a supervisory layer (responsible
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1 for the controller reconfiguration). In the particular case analyzed, controller reconfiguration
2 and use of multiple catalysts are needed to enlarge the range of MI and XS values of the final
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4 resins and also to overcome hard process constraints, such as maximum feed rate and reactor
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6 temperature values.
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9 Simulation results indicated that the proposed control strategy leads to stable reactor
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11 operations and to proper control of the final polymer properties. For this reason, it can be said
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13 that control reconfiguration represents an alternative to overcome existing operation limits
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15 and recover operability when multiple catalysts are used at plant site. As shown through
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17 simulation, it was observed that feed transition policies are particularly important during the
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19 catalyst exchange procedures, in order to prevent sharp transients caused by the distinct
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21 sensitivities of the different catalysts to modification of reaction temperatures and
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23 modification of hydrogen, cocatalyst and electron donor concentrations. Finally, it was shown
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25 that the scheduling task can be combined with control reconfiguration schemes for design of
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27 grade transition trajectories and optimization of the process operation.
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33 34 35 **Acknowledgments** 36

37
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40 Brazil) for supporting this work and providing scholarship.
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Notation

$C_{p,M}, C_{p,Pol}, C_{p,w}$	heat capacities of propylene, polymer and water, $\text{cal}\cdot\text{Kg}^{-1}\cdot\text{K}^{-1}$.
ΔH	heat of reaction, $\text{cal}\cdot\text{Kg}^{-1}$.
K_c	proportional gain of the PI controllers.
k_c, k_p, k_{tH}, k_{tM}	kinetic constants for initiation, propagation, chain transfer to hydrogen and chain transfer to propylene, $\text{L}\cdot\text{mol}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$.
k_{ts}, k_d	kinetic constants for spontaneous chain transfer and site deactivation reactions, h^{-1} .
K_{XS}	model gain for XS correlation, dimensionless.
$\dot{m}_M, \dot{m}_H, \dot{m}_{TEA}, \dot{m}_{PEEB}$	input rates of propylene, hydrogen, TEA and PEEB, $\text{Kg}\cdot\text{h}^{-1}$.
$\dot{m}_S, \dot{m}_{Pol}, \dot{m}_{gas}$	output rates of slurry, polymer and unreacted volatile reagents discharge, $\text{Kg}\cdot\text{h}^{-1}$.
\dot{m}_{M_c}, \dot{m}_w	flow rates of condensate and coolant water, $\text{Kg}\cdot\text{h}^{-1}$.
\dot{m}_{Cat}	input rates of catalyst, $\text{mol}\cdot\text{h}^{-1}$.
Cat, H_2, M	catalyst, hydrogen and propylene molar concentrations, $\text{mol}\cdot\text{L}^{-1}$.
M_c, M_{cw}	total mass in the condenser and in the coolant jacket, Kg.
MI	melting index of the final resin, $\text{g} (10 \text{ min})^{-1}$.
Mn, Mw	number-average and weight-average molecular weights, $\text{g}\cdot\text{mol}^{-1}$.
PD	polydispersity index, dimensionless.
$PEEB, Pol, TEA,$	PEEB (para-ethoxy ethyl benzoate), polymer and TEA (triethyl-
	aluminium) masses in the reactor, Kg.
$PM_H, PM_M,$	hydrogen and propylene molecular weights, $\text{g}\cdot\text{mol}^{-1}$.
R_{Pol}	rate of polymerization, $\text{Kg}\cdot\text{h}^{-1}$.
T_c	condensate temperature, K.
T_e, T	temperatures in the reactor feeding and output rates, K.

1	T_{we}, T_w	temperatures of input and output coolant water flow, K.
2	t_{rec}, t_{set}	instant time of catalyst exchange and grade implementation
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4	UA	global heat transfer coefficient, $\text{cal}\cdot\text{K}^{-1}\cdot\text{h}^{-1}$.
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6	V	reactor volume, L.
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9	w_M, w_{Pol}	propylene and polymer concentrations in the reactor, wt/wt.
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12	XS	fraction of the final resin extractable in xylene, % wt/wt.
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14	XS^R	extractable in xylene reference value, % wt/wt.
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20	Greek letters	
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22	α	tuning parameter of the first-order filter, dimensionless.
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24	δ	parameter for heat capacity and latent heat of vaporization of
25		propylene, dimensionless.
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29	λ_M	latent heat of vaporization of propylene, $\text{cal}\cdot\text{Kg}^{-1}$.
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32	$\lambda_{k,j}$	k-order moment for live polymer from the catalyst j.
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35	$\mu_{k,j}$	k-order moment for dead polymer from the catalyst j.
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38	ρ_M, ρ_{Pol}, ρ	propylene, bulk polymer and reaction mixture densities, $\text{Kg}\cdot\text{L}^{-1}$.
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41	τ_I	integral gain in the PI controllers, h.
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46	Indexes	
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48	j	represents the catalysts, $j = 1, 2, 3$.
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51	k	represents the order of polymer moments, $k = 0, 1, 2$.
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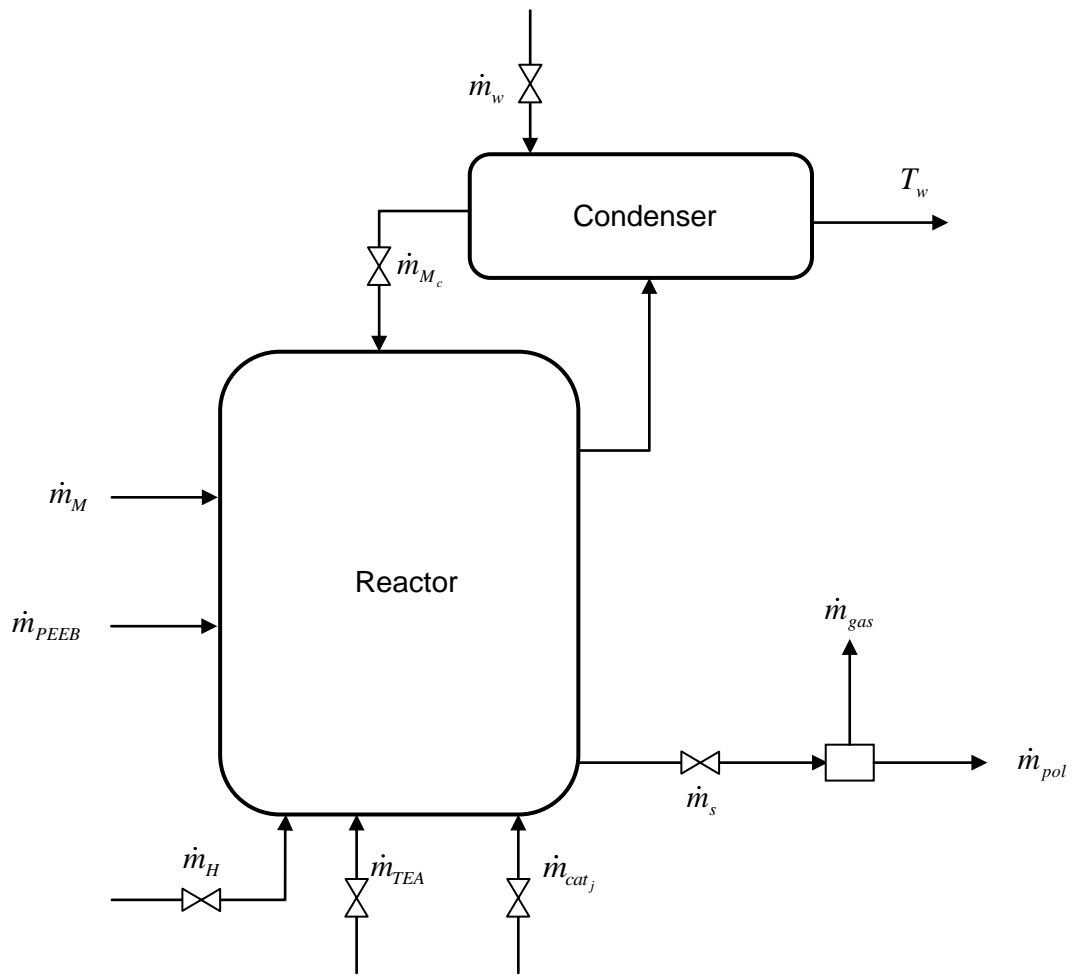


Figure 1. Simplified diagram of the polymerization reactor.

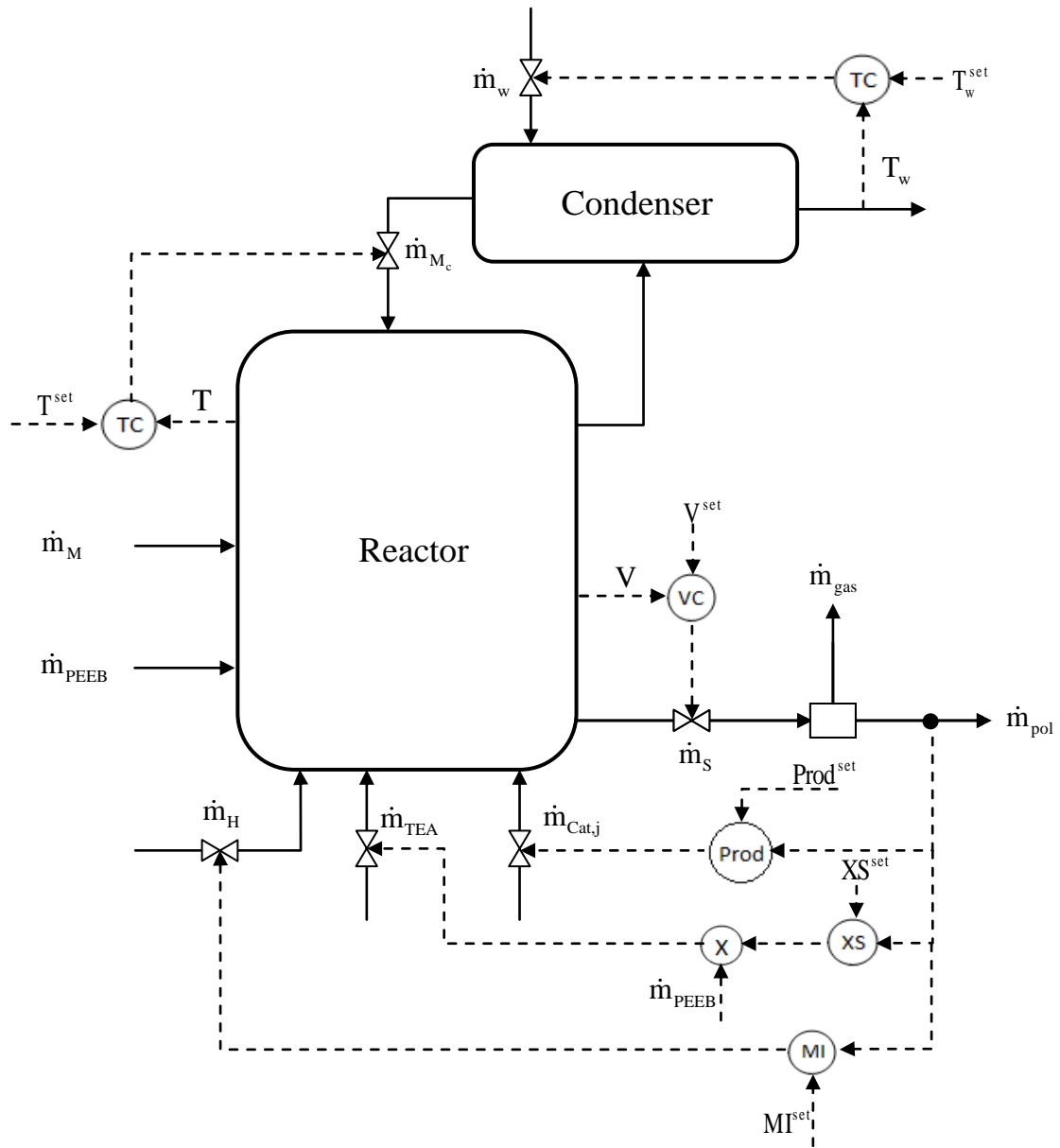


Figure 2-a. Representation of the control structure for operation with the Ziegler-Natta catalysts (Cat₁ e Cat₂).

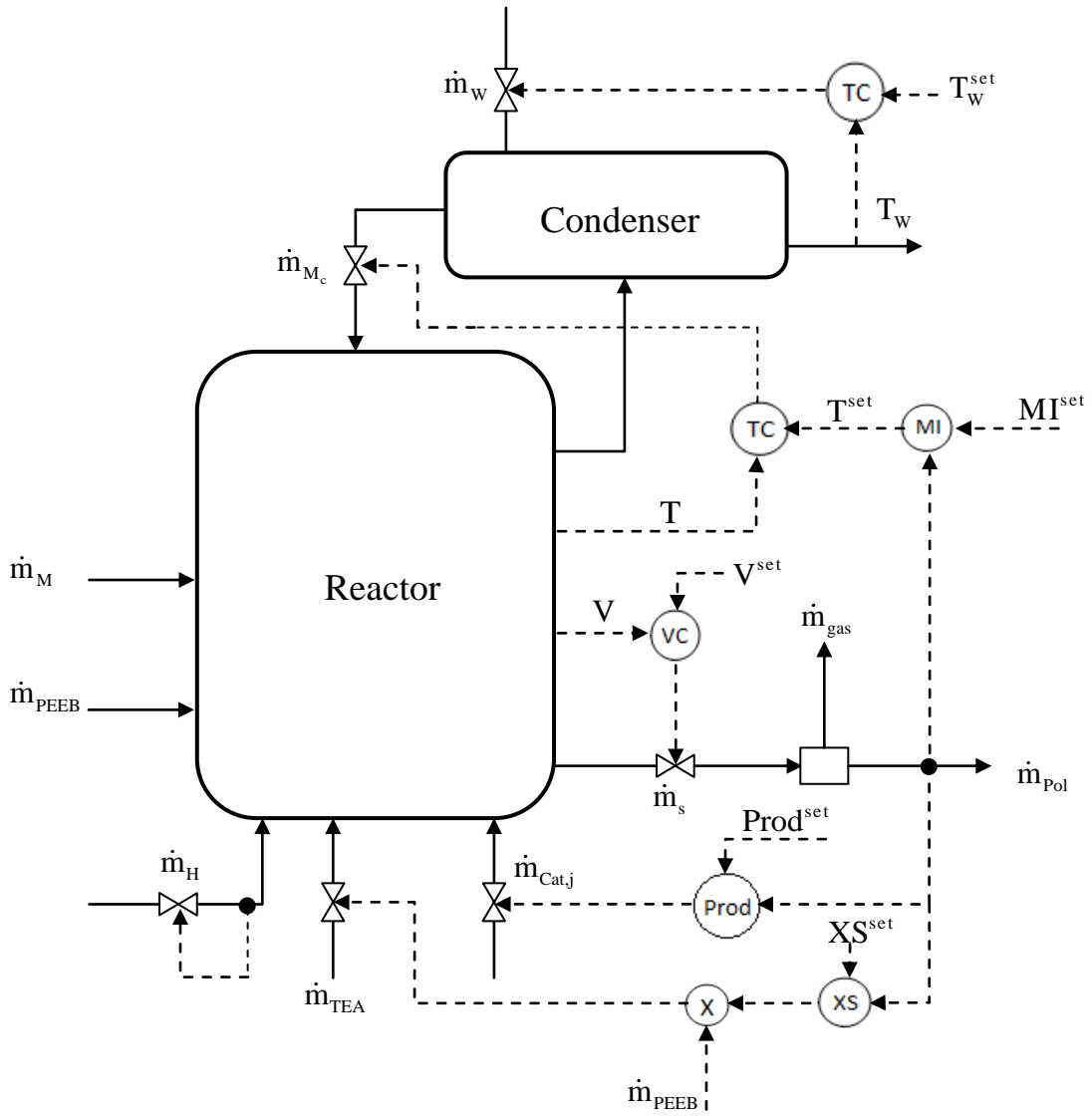


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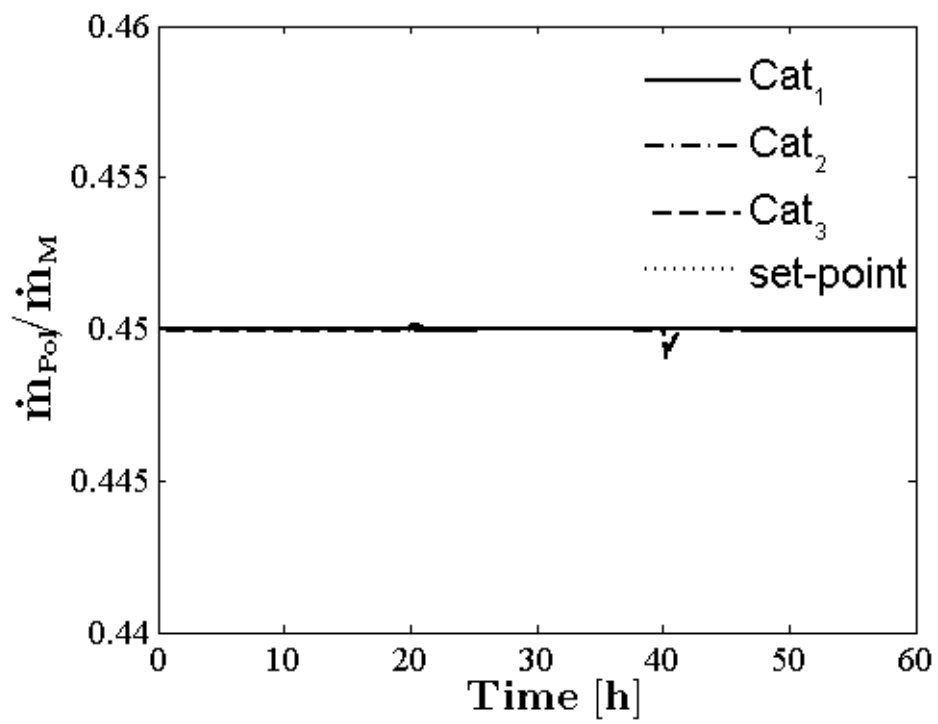


Figure 3-a. Process productivity during the MI transition with a single catalyst.

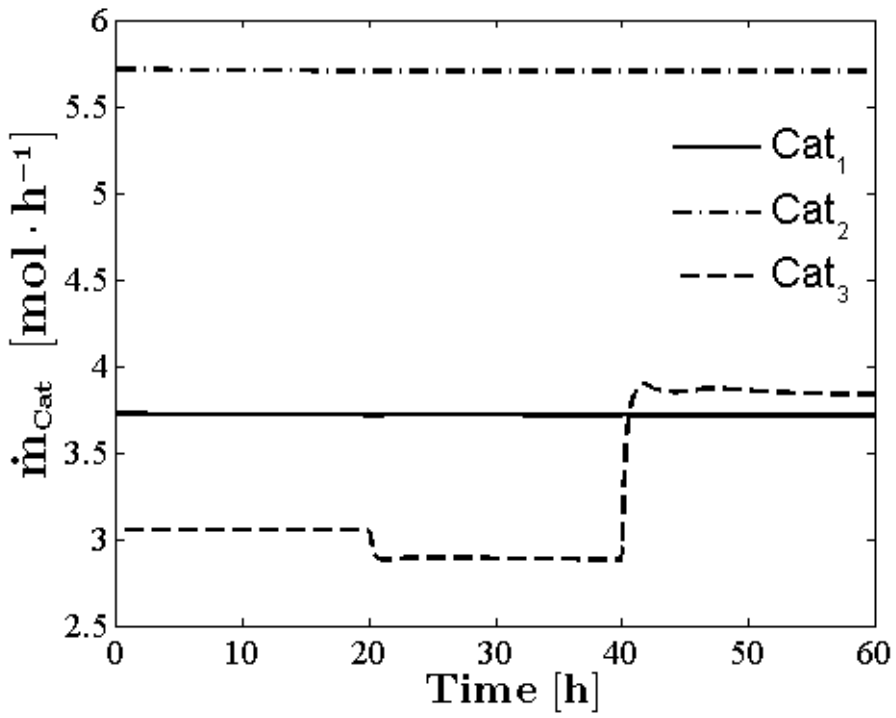


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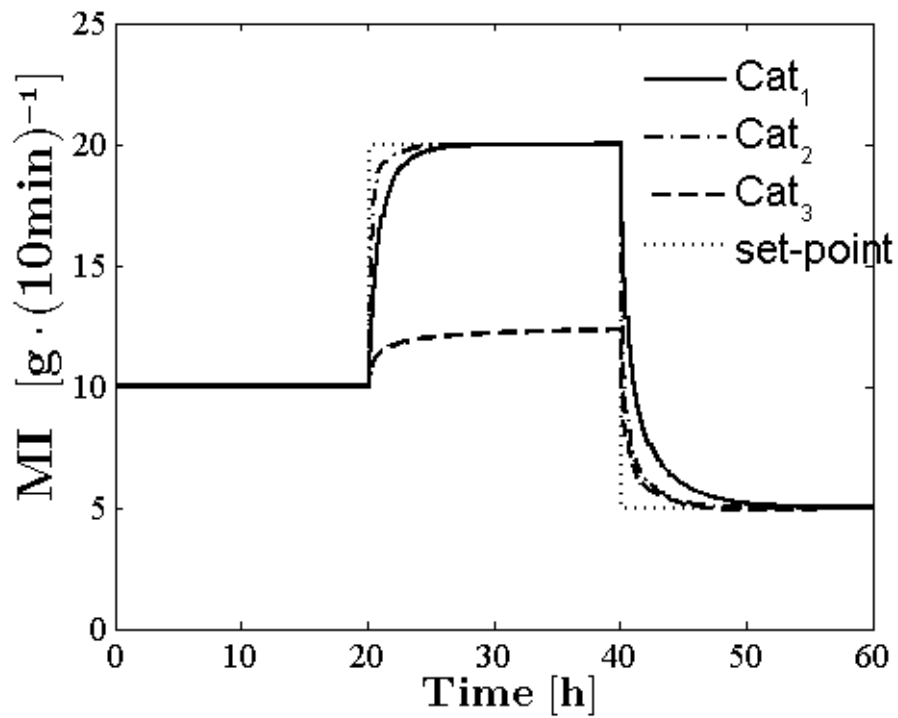


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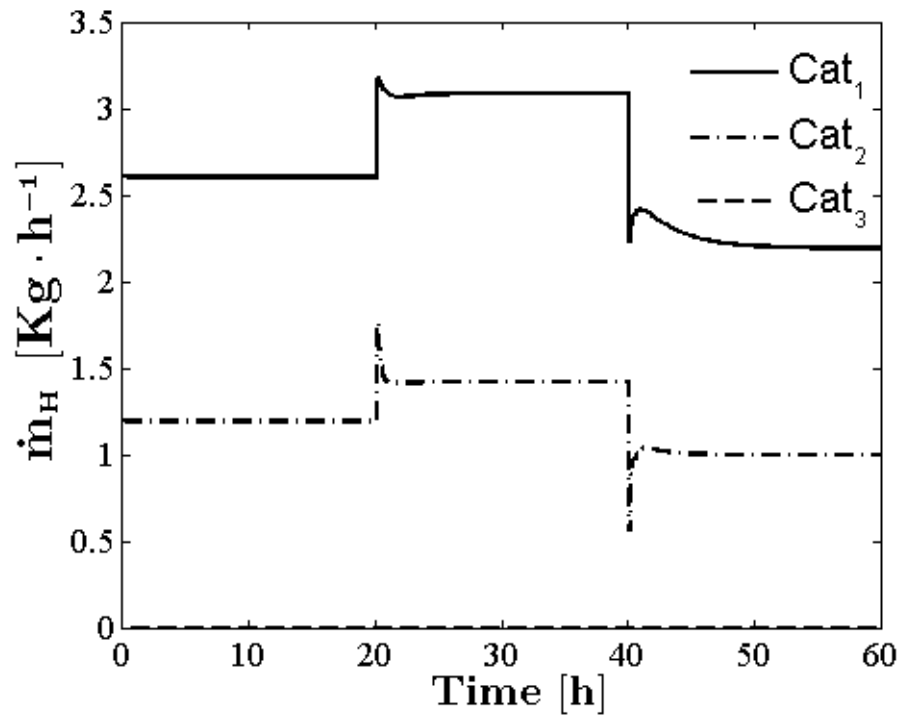


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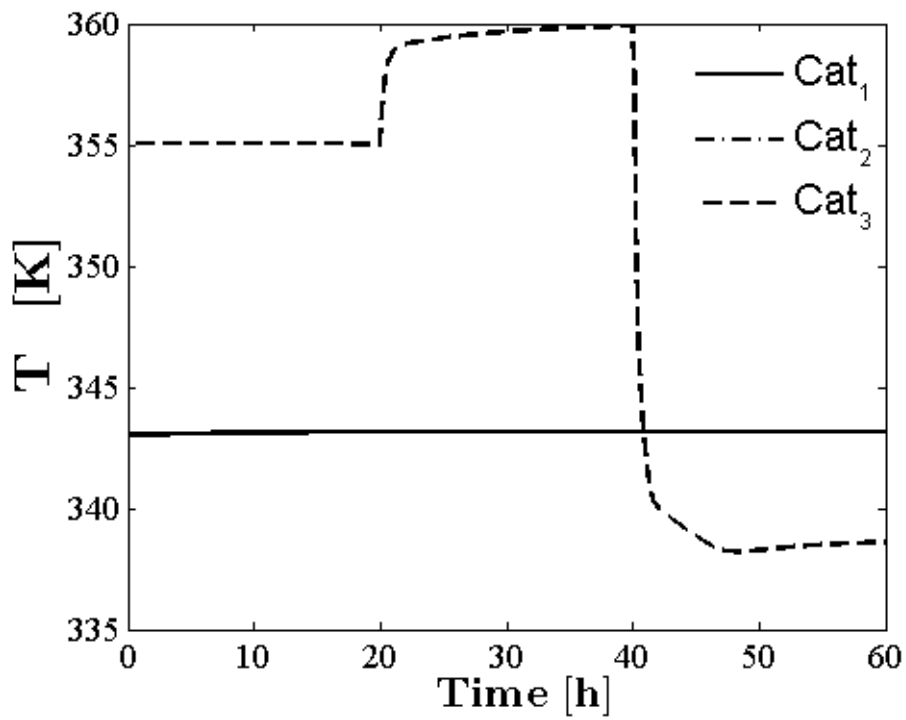


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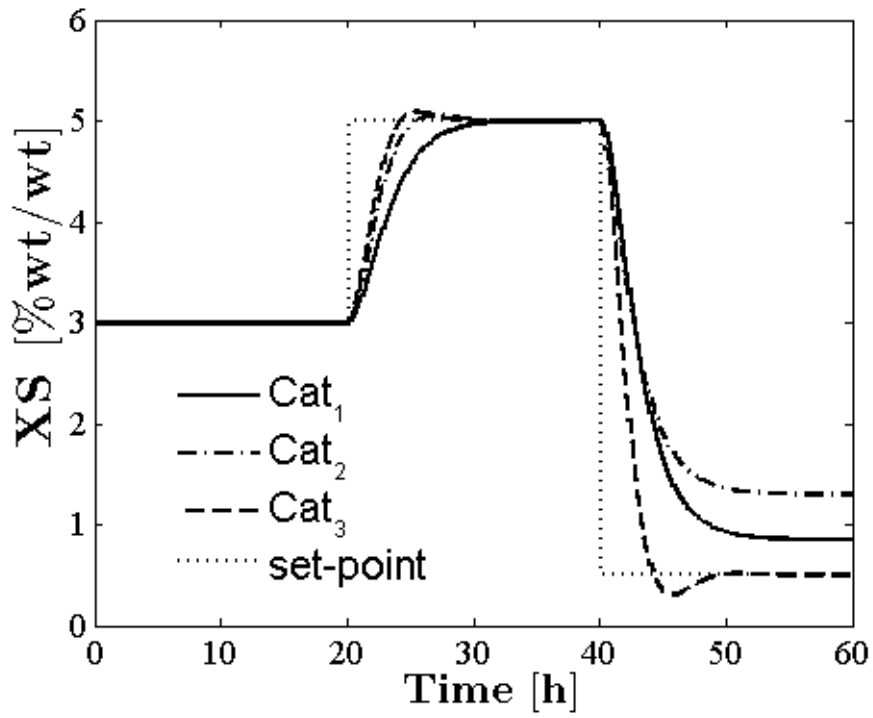


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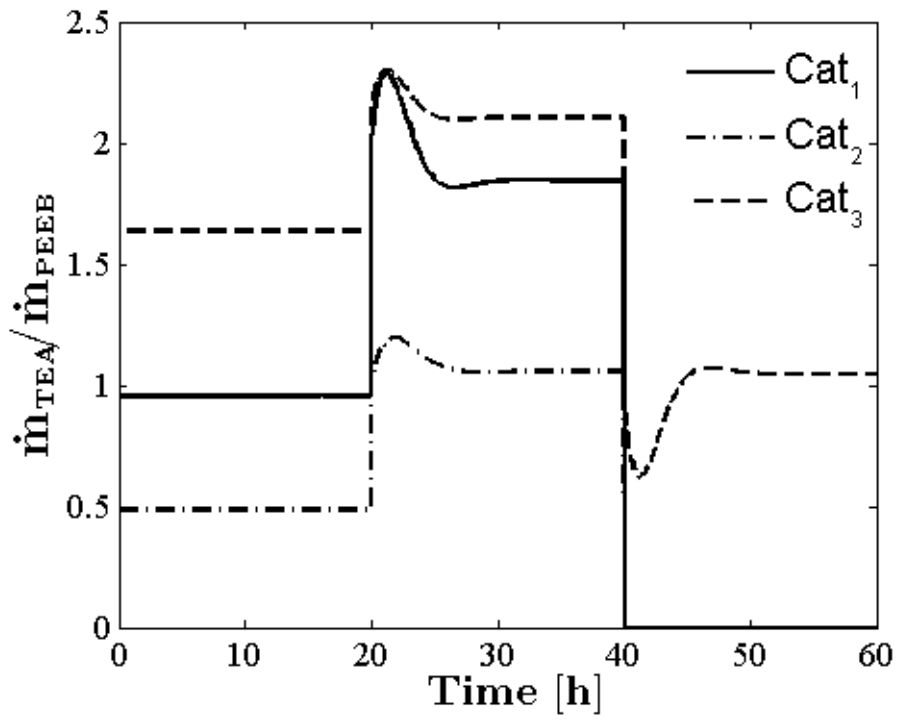


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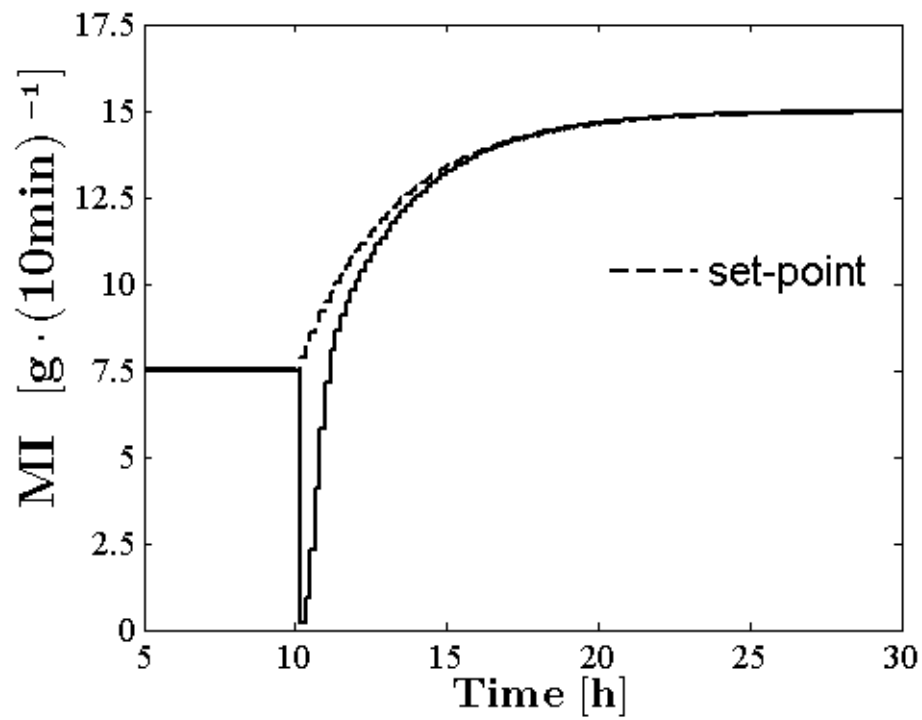


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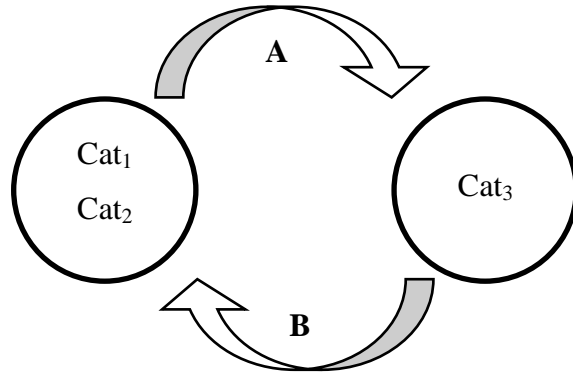


Figure 5. Simplified schematic representation for the catalyst exchange in line.

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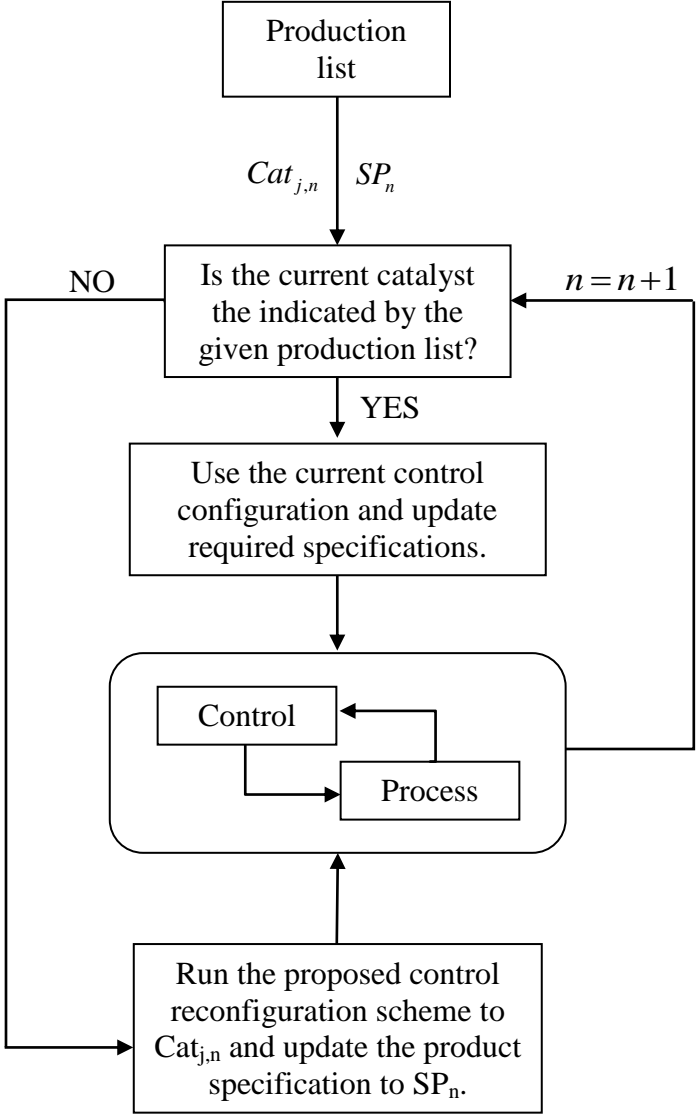


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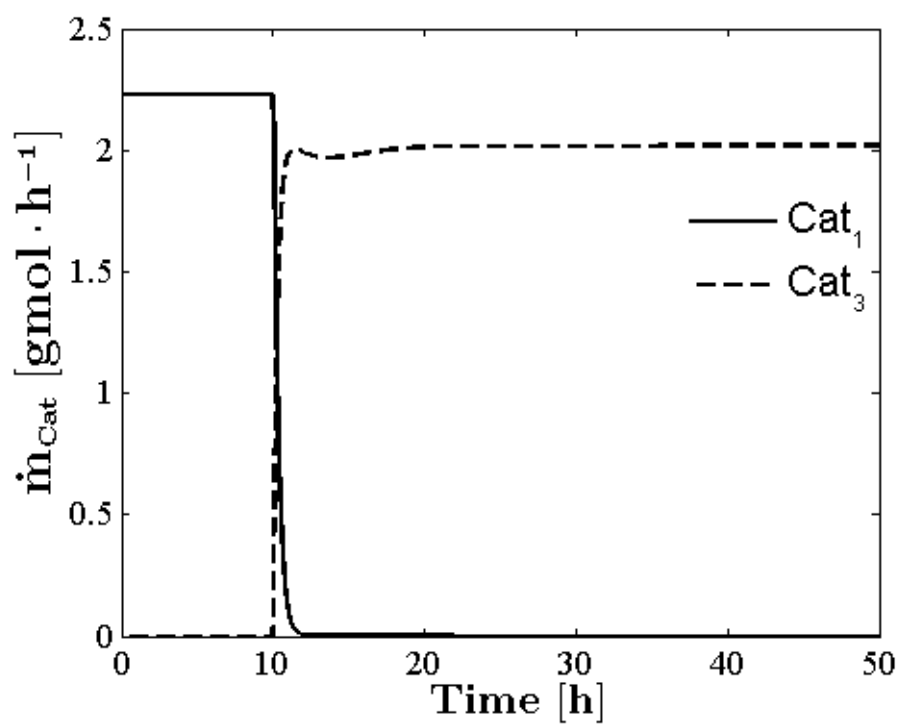


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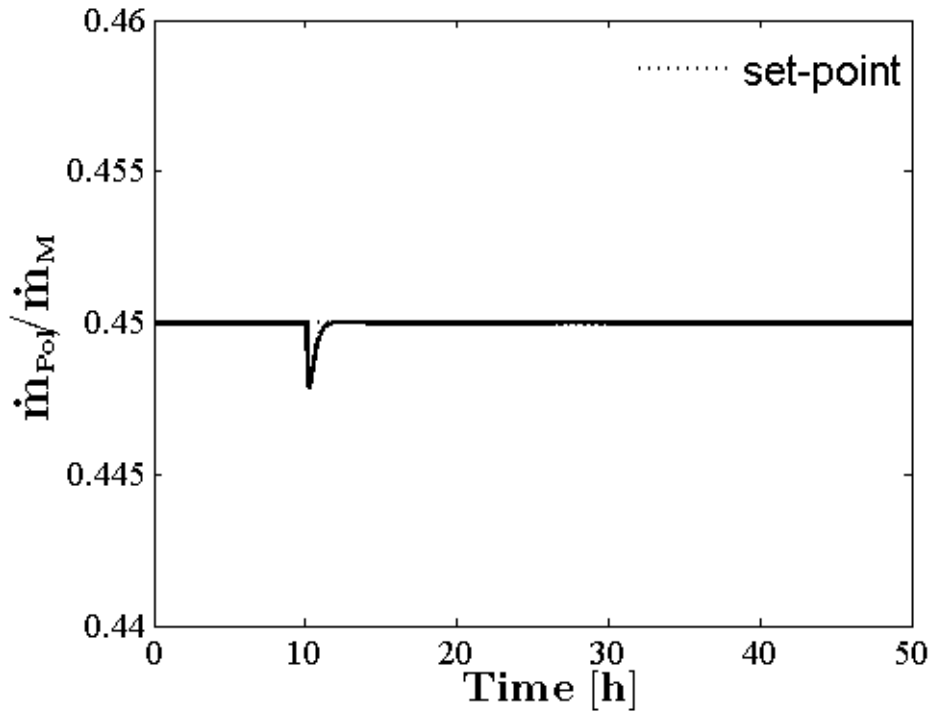


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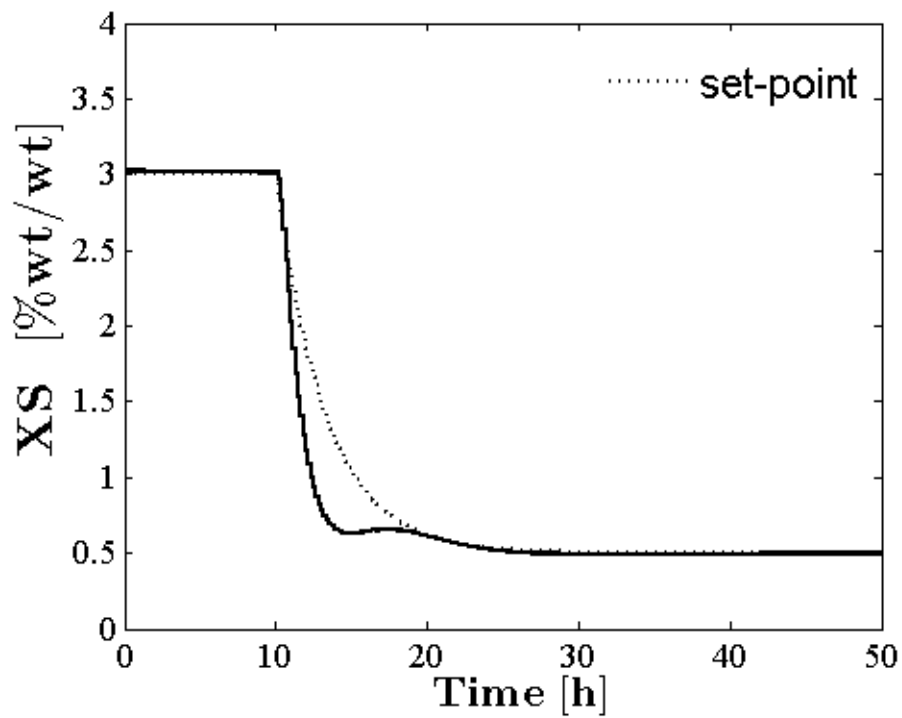


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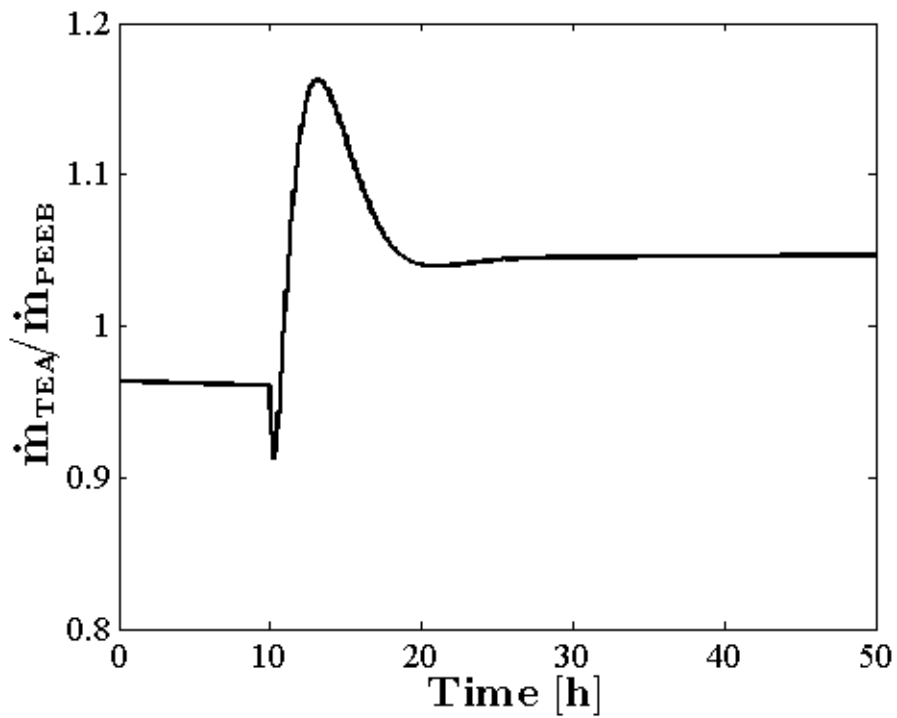


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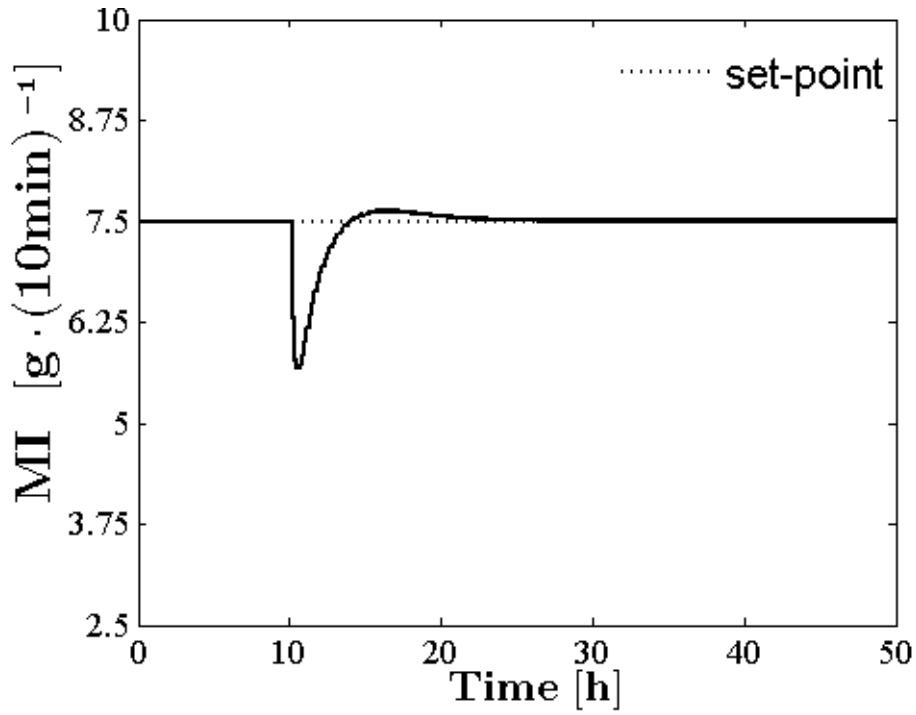


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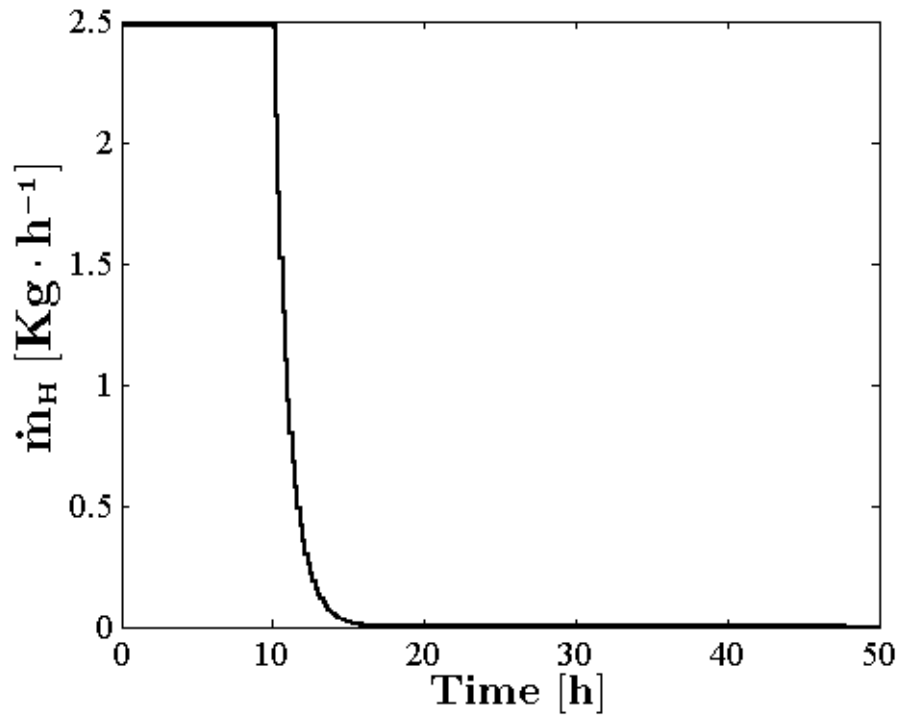


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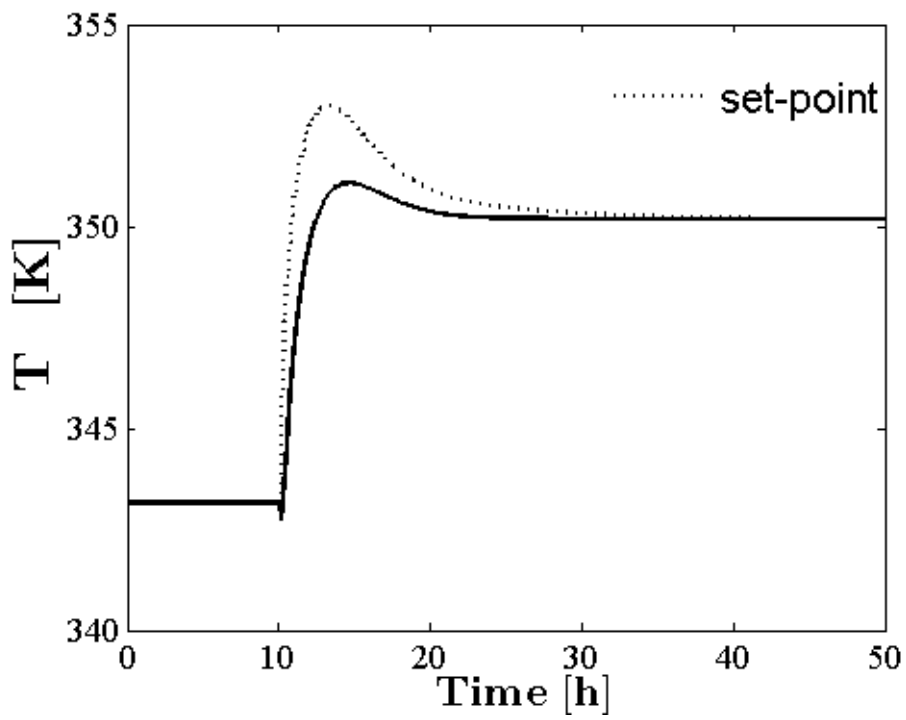


Figure 7-g. Manipulation of the reactor temperature to control MI in the test Cat_1 - Cat_3

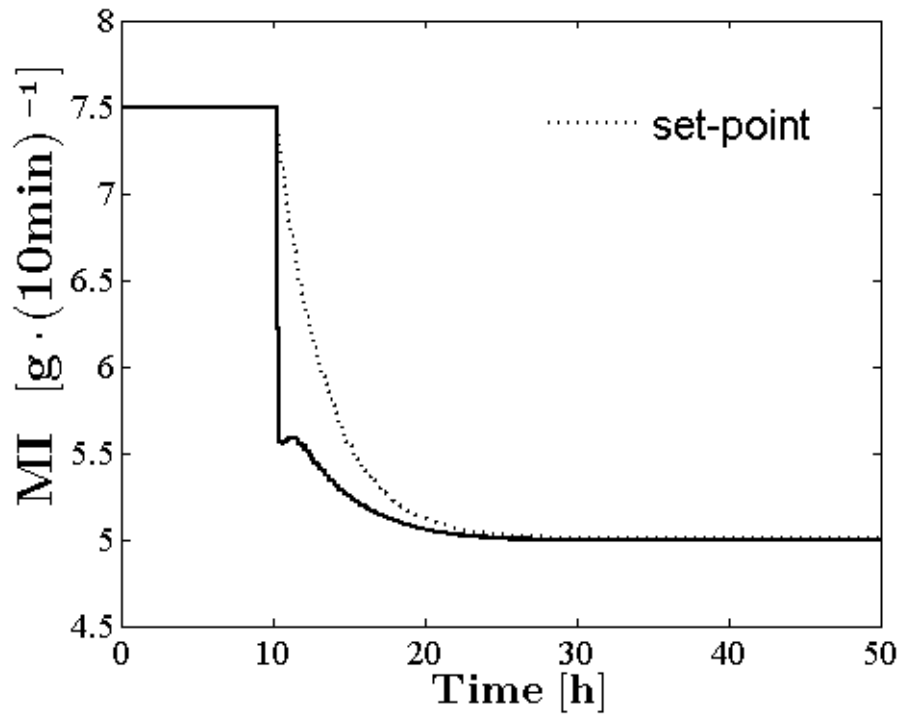


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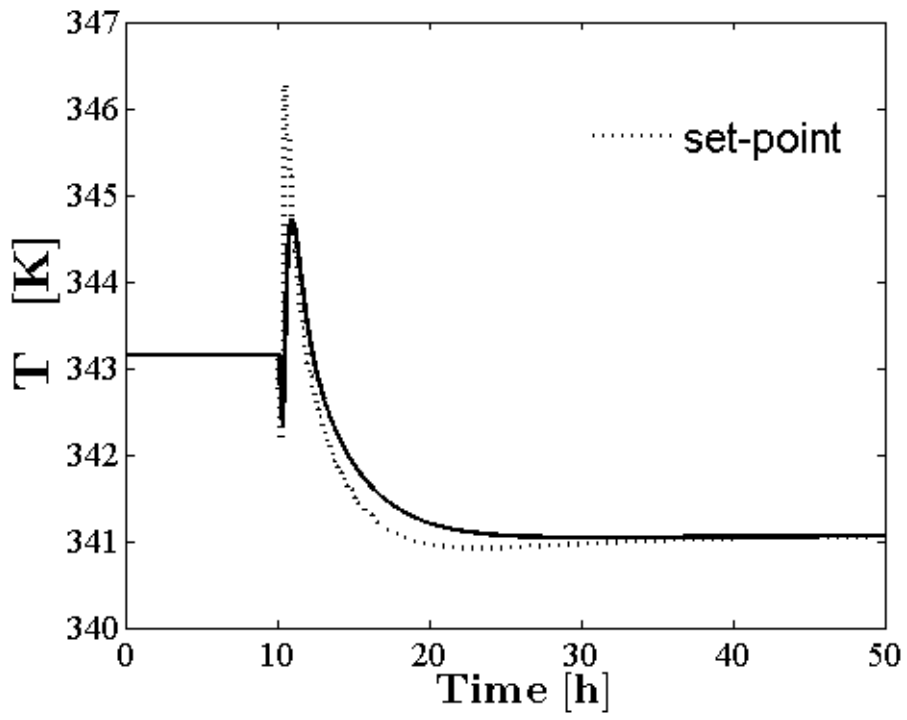


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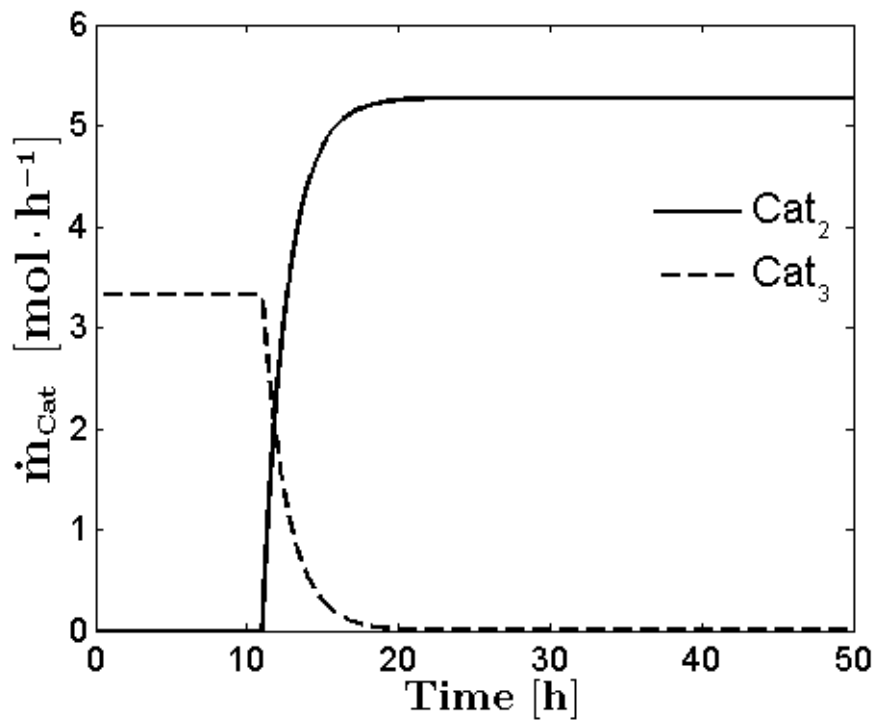


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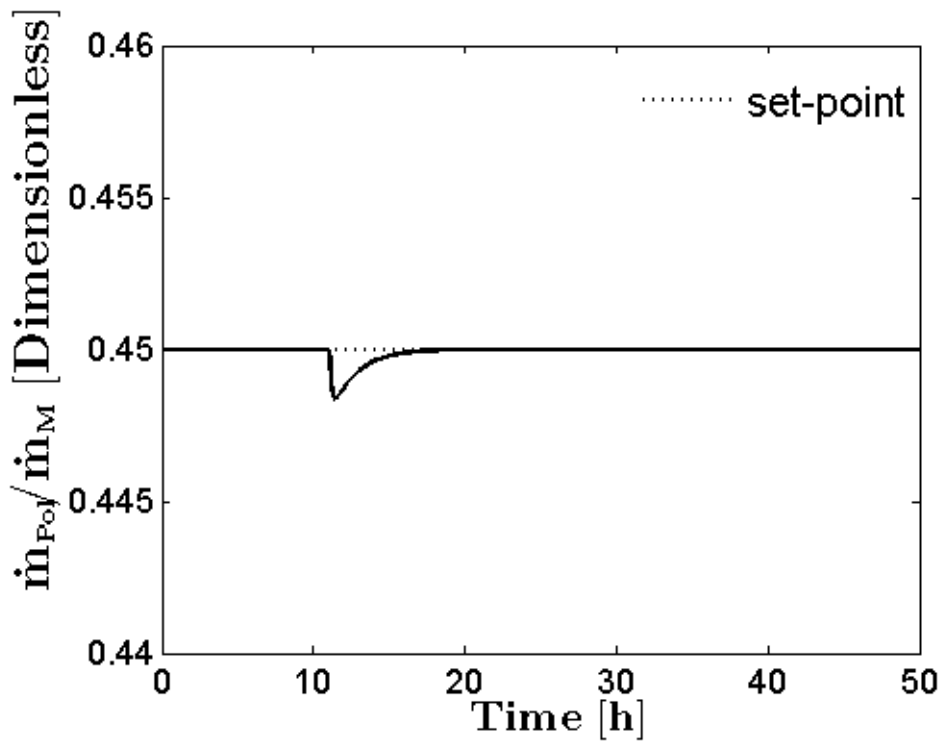


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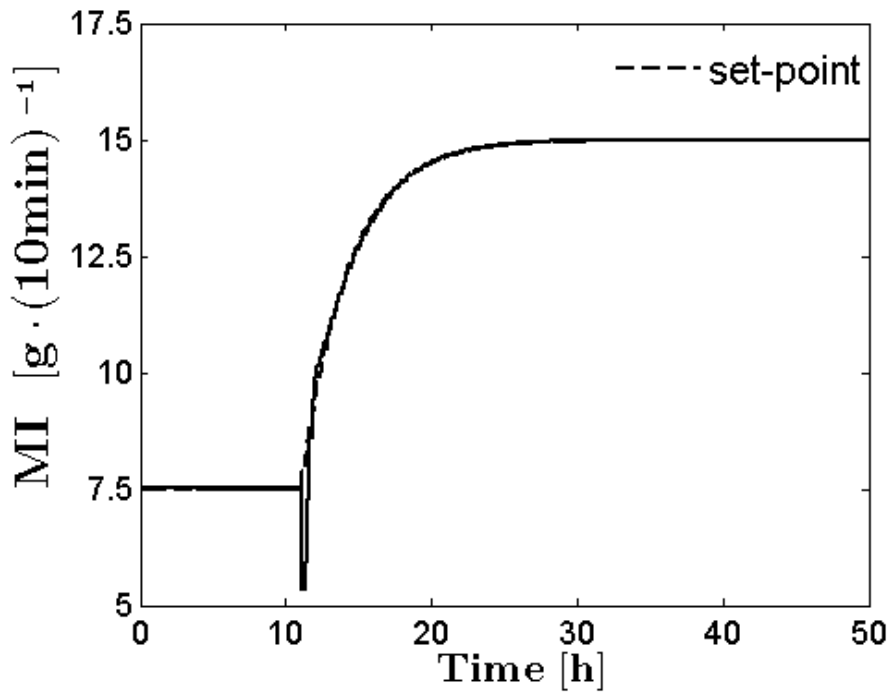


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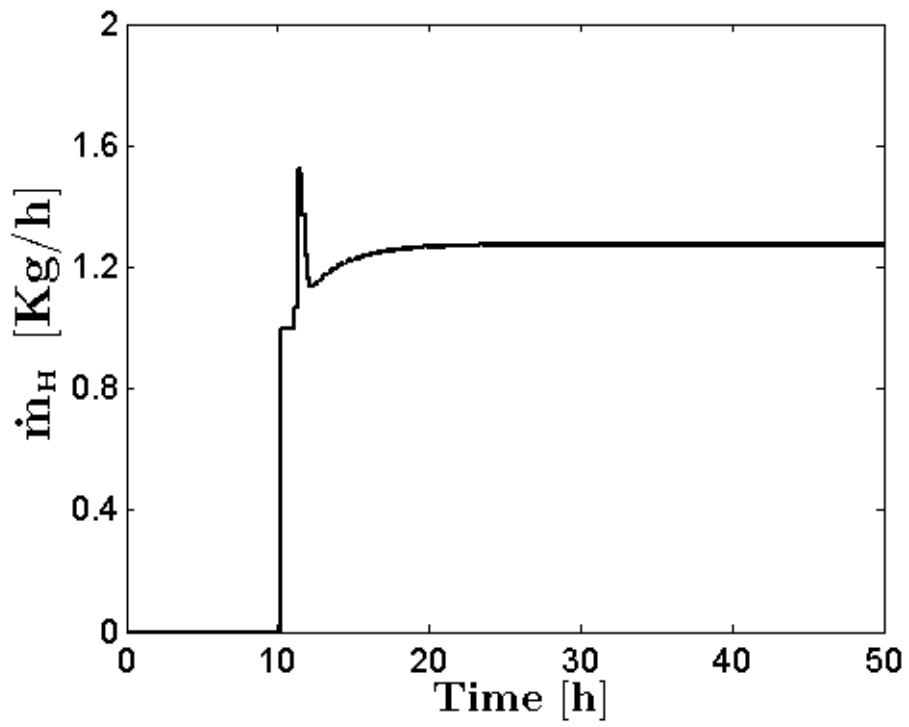


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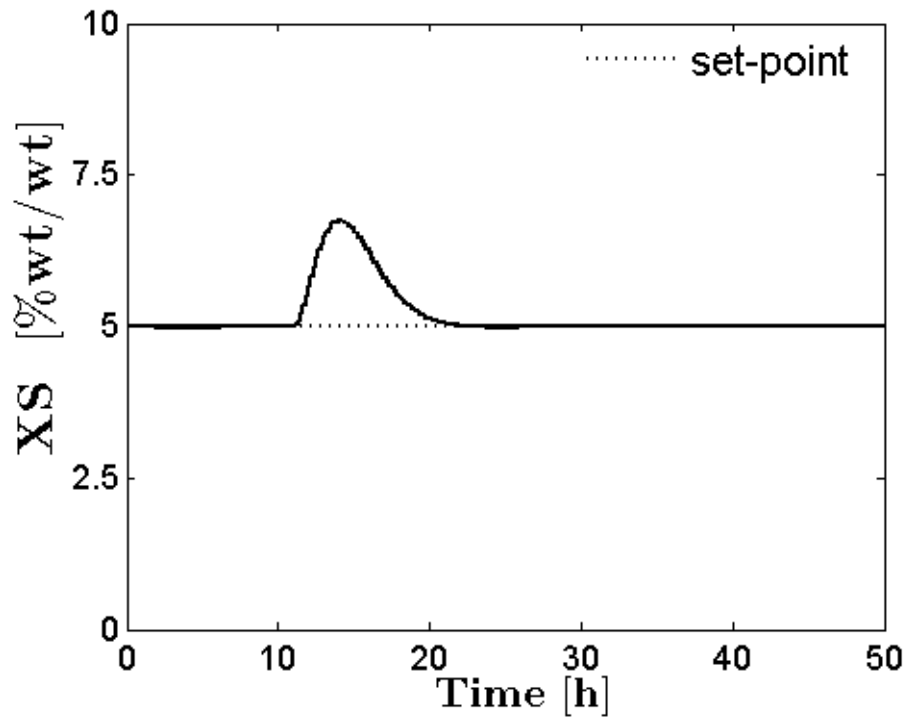


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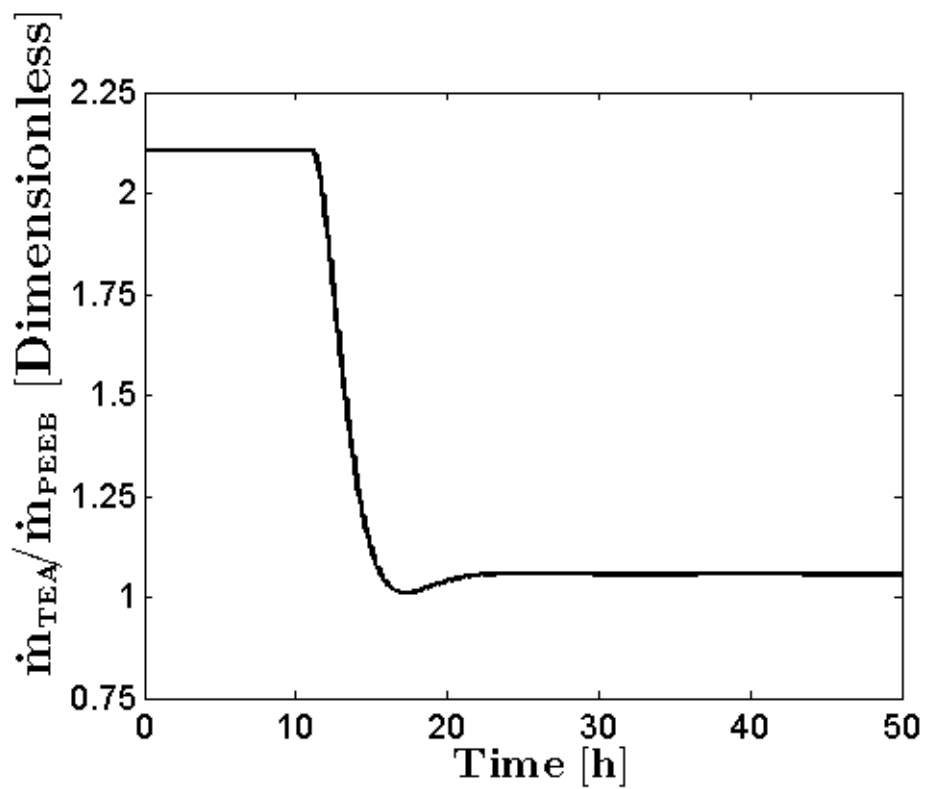


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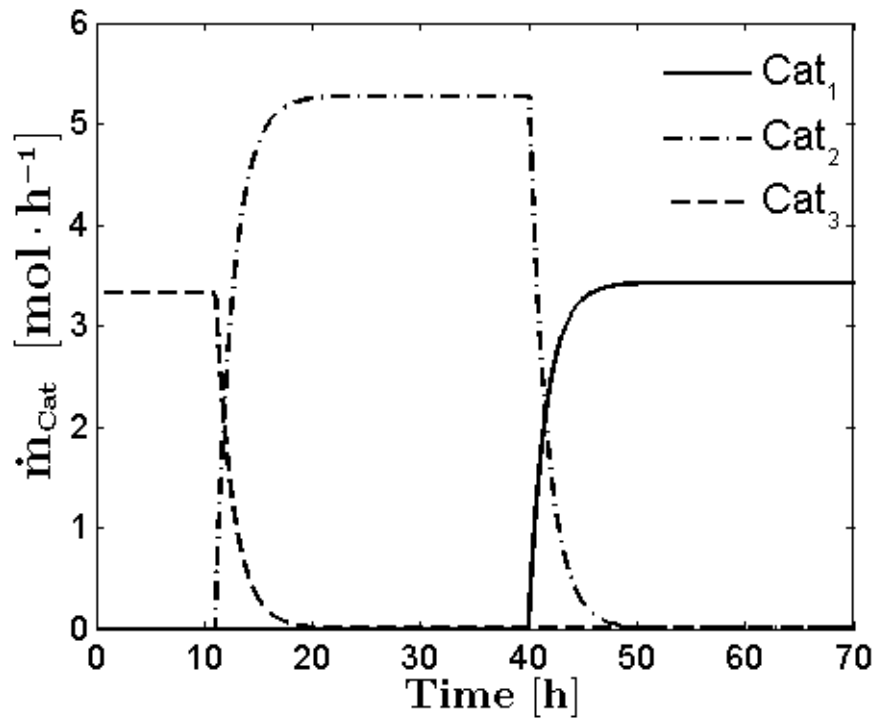


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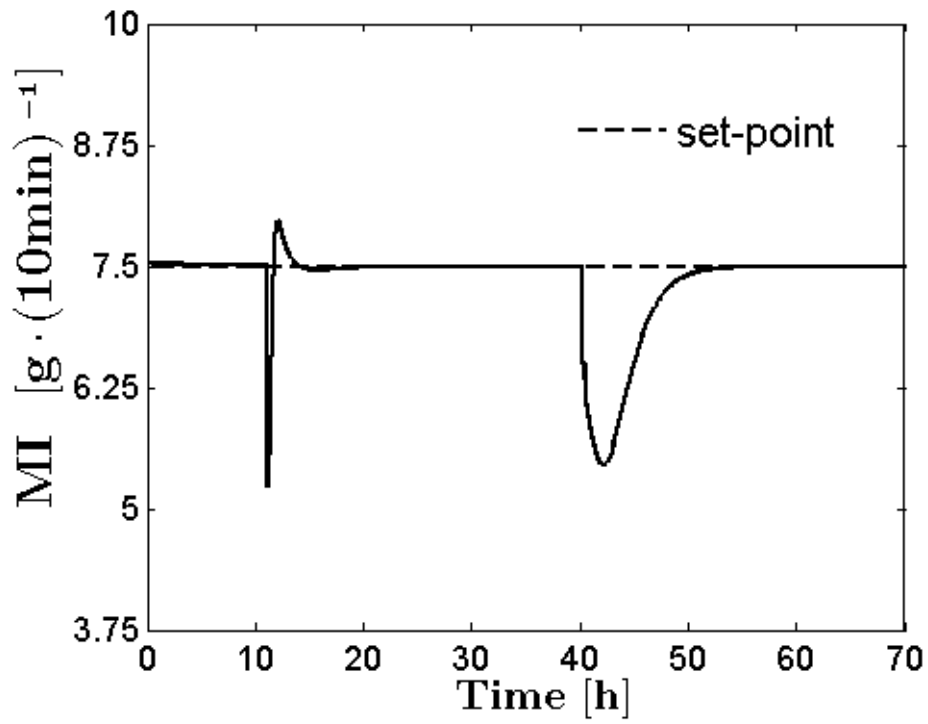


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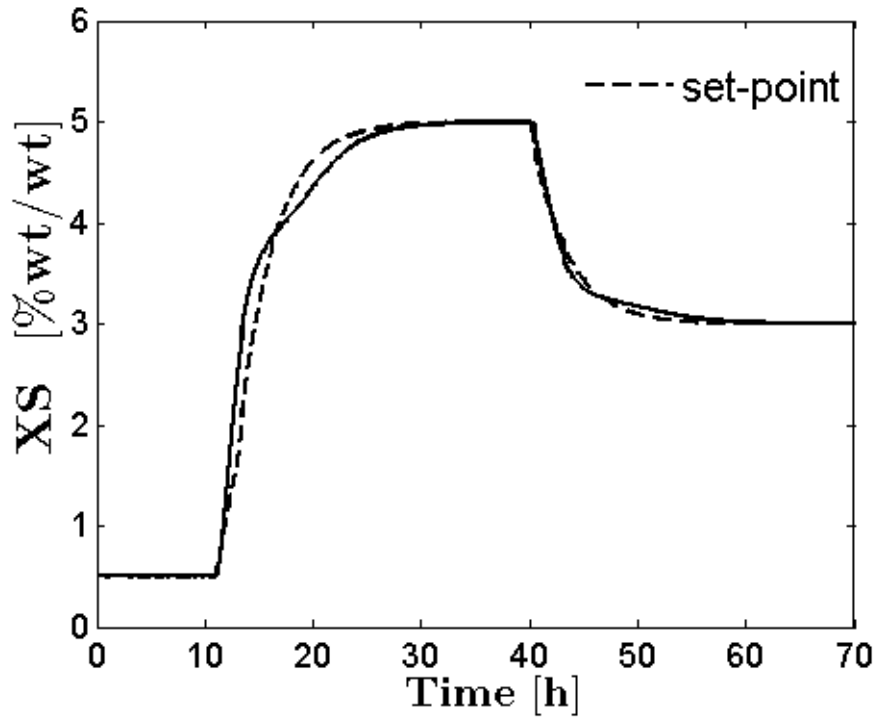


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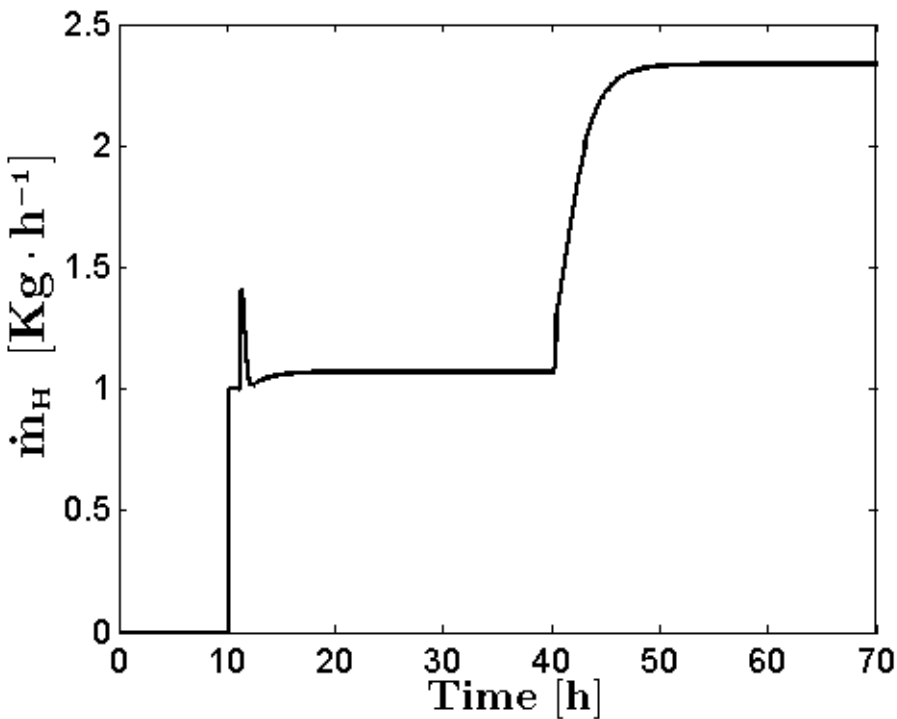


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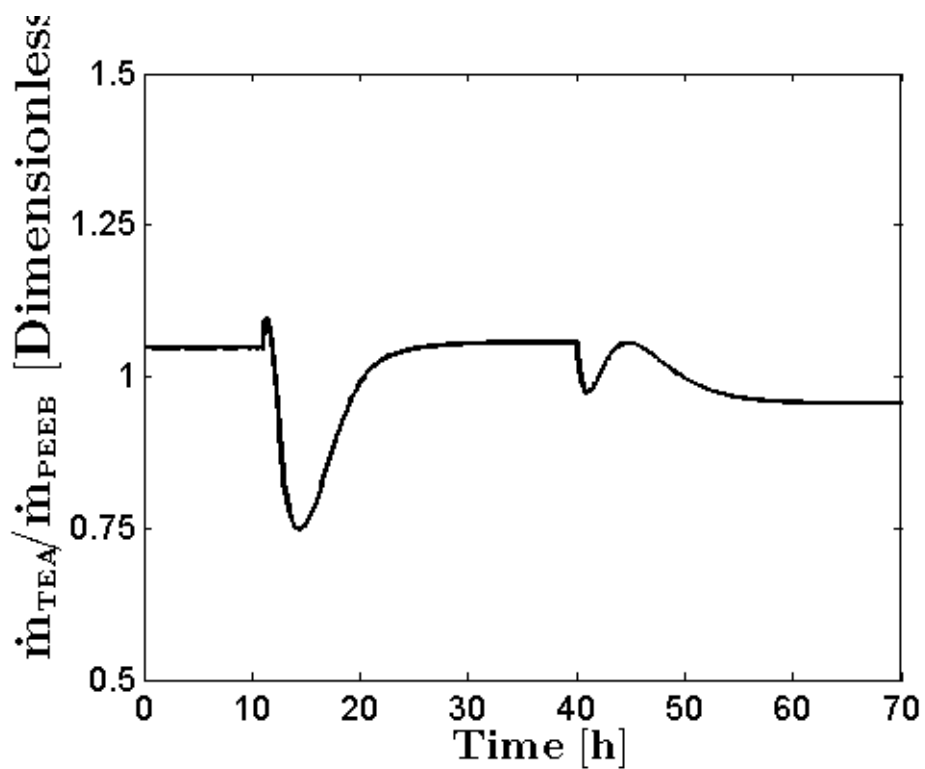


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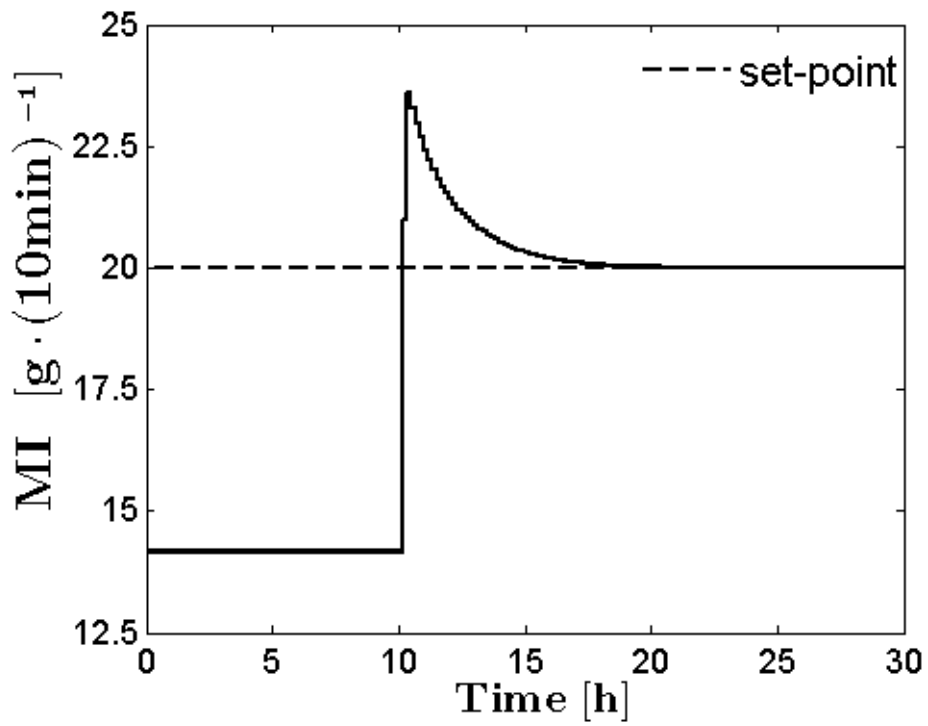


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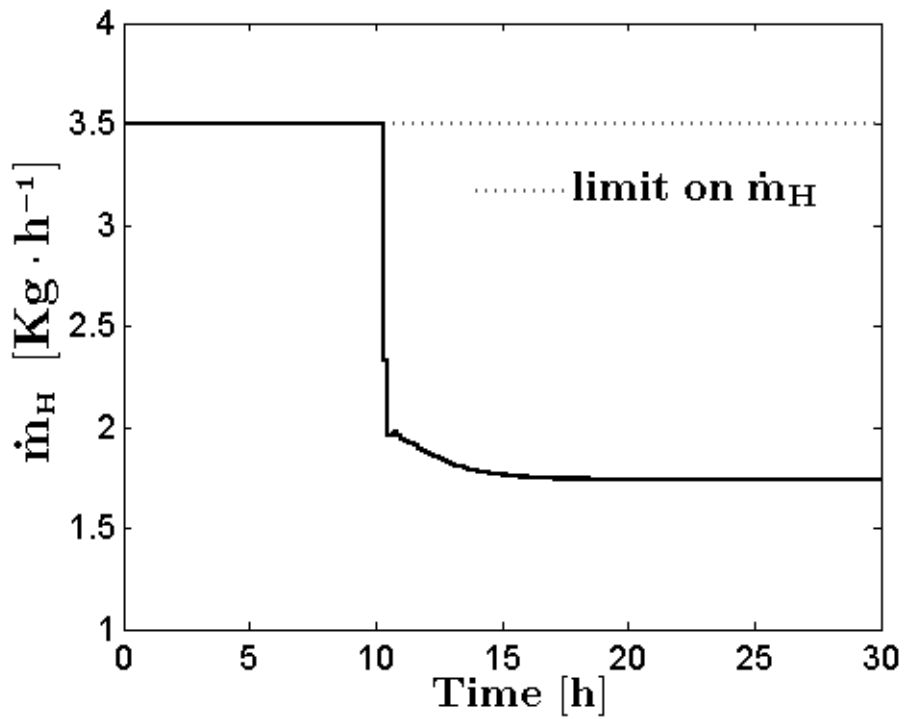


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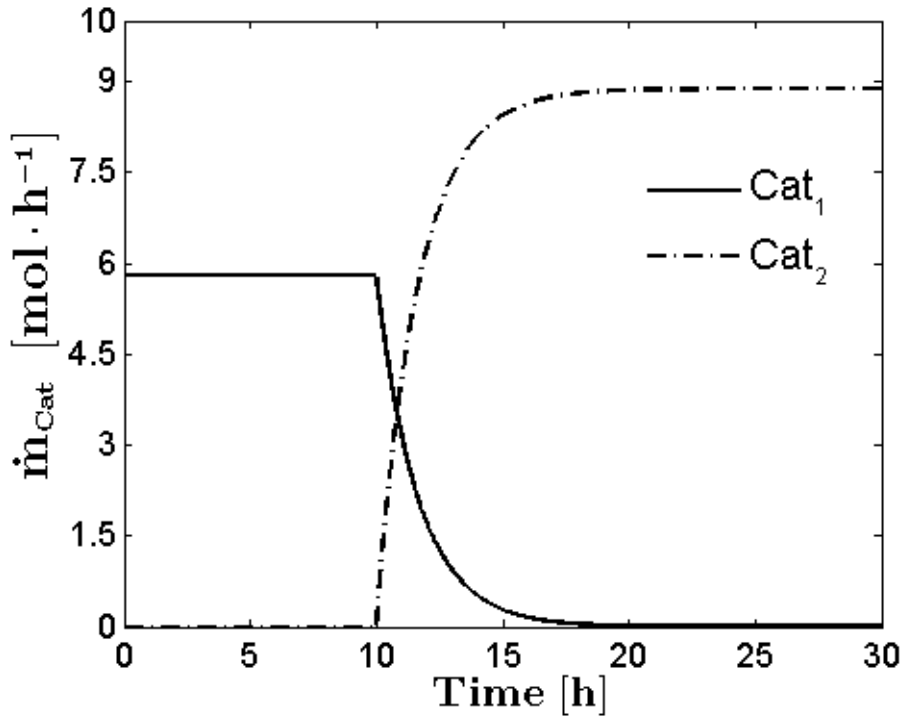


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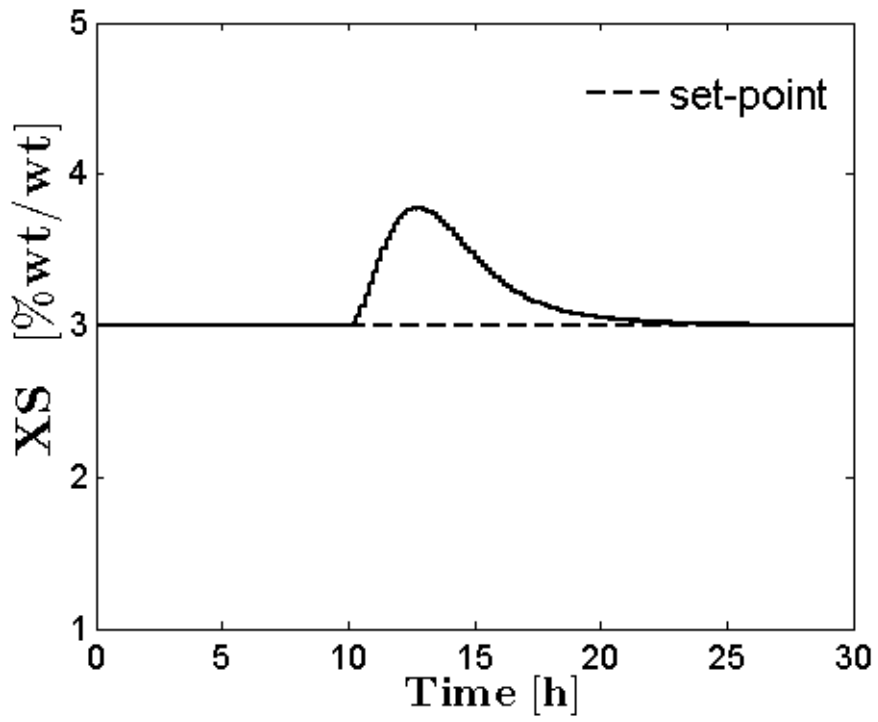


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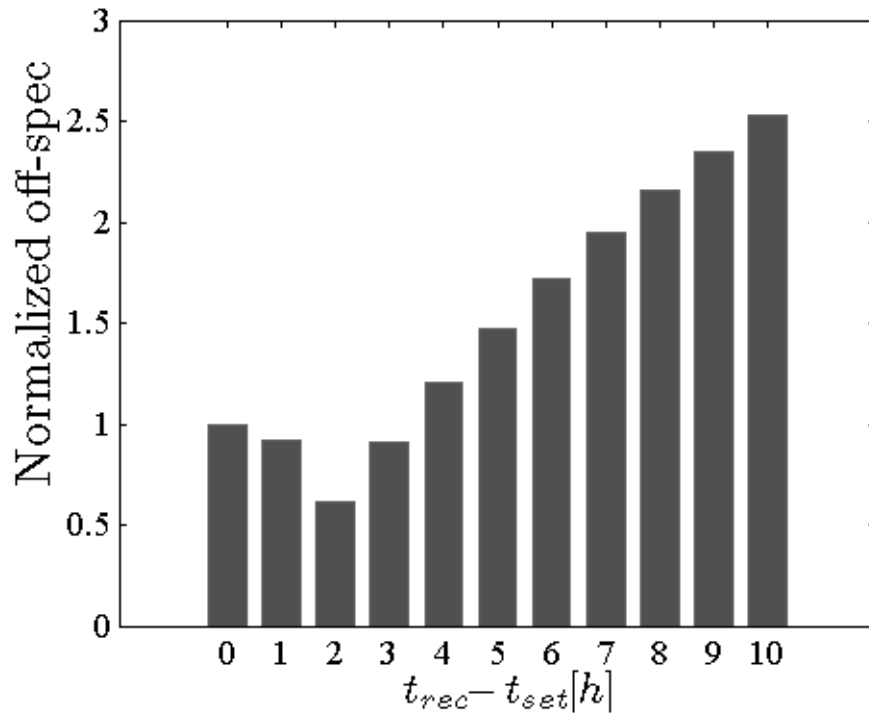


Figure 11. Normalized off-spec product amount for different instant times of catalyst exchange (t_{rec}) from the time of implementation of the set point (t_{set}).

List of tables

Table 1: Catalysts used in the polymerization and the expected polymer properties.

Catalyst	Type	Polymer final properties
1	Ziegler-Natta	High molecular weight and high XS
2	Ziegler-Natta	Low molecular weight e high XS
3	Metallocene	High molecular weight and low XS

Observation: XS indicates the fraction of polymer extracted by boiling xylene.

Table 2: Summary of the proposed kinetic model for the polymerization of propylene.

Step	Reaction	Rate	Catalyst		
			1	2	3
Chain initiation	$C_j + M \xrightarrow{k_{c,j}} P_{1,j}$	$R_{c,j} = k_{c,j} M C_j$	●	●	●
Chain propagation	$P_{i,j} + M \xrightarrow{k_{p,j}} P_{i+1,j}$	$R_{p,j} = k_{p,j} M P_{i,j}$	●	●	●
Chain transfer	$P_{i,j} + H_2 \xrightarrow{k_{tH,j}} D_{i,j} + C_j$	$R_{tH,j} = k_{tH,j} H_2 P_{i,j}$	●	●	○
	$P_{i,j} + M \xrightarrow{k_{tM,j}} D_{i,j} + C_j$	$R_{tM,j} = k_{tM,j} M P_{i,j}$	○	●	○
	$P_{i,j} \xrightarrow{k_{ts,j}} D_{i,j} + C_j$	$R_{ts,j} = k_{ts,j} P_{i,j}$	○	○	●
Site deactivation	$P_{i,j} \xrightarrow{k_{d,j}} D_{i,j}$	$R_{d,j} = k_{d,j} P_{i,j}$	○	●	●

Observation: (1) The symbol “●” points out to the presence of a certain kinetic step in the reaction of the catalyst j, while “○” means its absence, where j = 1, 2 e 3. (2) The constants $k_{c,j}$, $k_{p,j}$, $k_{tH,j}$, $k_{ts,j}$, $k_{tM,j}$ and $k_{d,j}$ are represented by Arrhenius type expressions, depending on the reaction temperature.

Table 3: Kinetic parameters for the propylene polymerization reactions.

Step	Activation energy [10 ³ cal·Kg ⁻¹]		Pre-exponential factor		Catalyst		
					1	2	3
Initiation	E _c	5,0	k _{c0}	[L·mol _{cat} ⁻¹ ·h ⁻¹]	1·10 ⁴	1·10 ⁴	1,2·10 ⁴
Propagation	E _p	5,0	k _{p0}	[L·mol _{cat} ⁻¹ ·h ⁻¹]	7,5·10 ³	5·10 ³	8,15·10 ³
Transfer	E _{tH}	7,0	k _{tH0}	[L·mol _{cat} ⁻¹ ·h ⁻¹]	5·10 ²	7,5·10 ²	-
	E _{tM}	7,0	k _{tM0}	[L·mol _{cat} ⁻¹ ·h ⁻¹]	-	27,5	-
	E _{ts}	7,0	k _{ts0}	[h ⁻¹]	-	-	18,5
Deactivation	E _d	7,0	k _{d0}	[h ⁻¹]	-	2,0·10 ⁻²	5,0·10 ⁻²

Table 4: Process parameters used in simulation.

Parameter	Description	Value	
M_c	total mass in the condenser	1·10 ³	Kg
M_{cw}	total mass in the coolant jacket	1·10 ³	Kg
PM_H	Hydrogen molecular weight	2.0	g·mol ⁻¹
PM_M	propylene molecular weight	42.08	g·mol ⁻¹
R	Universal gas constant	1.987	cal·mol ⁻¹ ·K ⁻¹
T_{ref}	Reference temperature	343.15	K
UA	heat transfer global coefficient	5.5·10 ³	Kcal·K ⁻¹ ·h ⁻¹
ΔH	Heat of propagation reaction	-142·10 ³	cal·Kg ⁻¹

Table 5: Additional parameters for the catalysts.

Parameter	Catalyst		
	1	2	3
X _S _R [% wt/wt]	3.10	4.80	0.30
K _X _S [dimensionless]	2.25	3.50	4.25

Table 6: Operational constraints for the process variables.

Variable	Lower bound	Upper bound
\dot{m}_H	0	3.5
\dot{m}_w	0	$4.0 \cdot 10^4$
\dot{m}_{M_c}	0	$1.5 \cdot 10^6$
T	335	360

Table 7: Tuning for the proportional and integral gains in the controllers.

Parameter	Control loops in configurations A and B						
	$V \leftrightarrow \dot{m}_S$	$T \leftrightarrow \dot{m}_{M_c}$	$T_w \leftrightarrow \dot{m}_w$	$XS \leftrightarrow \frac{\dot{m}_{YEA}}{\dot{m}_{PEEB}}$	Prod $\leftrightarrow \dot{m}_{Cat.j}$	MI $\leftrightarrow \dot{m}_H$	MI $\leftrightarrow T_{set}$
K_C	-10 ^{a)}	$-5 \cdot 10^2$ ^{b)}	$-1 \cdot 10^3$ ^{b)}	0.25 ^{c)}	0.015 ^{d)}	0.05 ^{e)}	2.5 ^{f)}
τ_I [h]	10	10	2.5	2.0	0.2	1.2	0.5

Observation: (1) the syntaxes $y \leftrightarrow u$ means that y is controlled by manipulating u . (2) the unity of the gain K_C for each loop is ^{a)} $\text{Kg} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$; ^{b)} $\text{Kg} \cdot \text{L}^{-1} \cdot \text{K}^{-1}$; ^{c)} dimensionless; ^{d)} $\text{mol} \cdot \text{h}^{-1}$; ^{e)} $10 \text{ min} \cdot \text{Kg} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$; and ^{f)} $10 \text{ min} \cdot \text{K} \cdot \text{g}^{-1}$. (3) the two last columns present the tunings for each MI control loop.

Table 8: Nominal polymer specification for the operation with each catalyst.

Catalyst	Melting index [g·(10 min) ⁻¹]	Xylene extractable [% wt/wt]
1	10	3.0
2	20	5.0
3	5	0.5

Table 9: Summary of the properties of the catalysts taken from the preliminary test.

Catalyst	Discussion
Cat ₁	This catalyst with Ziegler-Natta kinetics is indicated to produce polypropylene with broad range of melting index and stiffness. However, its use requires a large amount of hydrogen when compared to Cat ₂ . Regarding the stiffness, it is recommended when this property should be set on low to moderated values, once keeping the mass ratio TEA/PEEB around the unity suffices. This is adequate to avoid affecting the controllability in case there is fluctuation in PEEB feed rate.
Cat ₂	With Ziegler-Natta kinetics, this catalyst also makes available polymers with broad range of melting index and stiffness. As it uses less hydrogen to control the melting index is indicated when ones wants to reduce the usage of this component. With regard to stiffness, it preferably produces polymers with low values and, if it is required to increase this property, an important stationary offset will be able to take place.
Cat ₃	The catalyst with Metallocene kinetics seems to be suitable to produce polypropylene with low melting index and high stiffness. In fact, the need to maintain the reaction temperature at high values, so as to control the catalyst activity, is what limits the ability to increase the melting index. In regard to the stiffness, any value can be obtained; however, this can be costly as the consumption of cocatalyst may increase.

Table 10: Example of a production list for the polymerization reactor.

Instant (t_n)	t_0	t_1	t_2	...	t_n
Catalyst (Cat _{j,n})	Cat _{1,0}	Cat _{3,1}	Cat _{2,2}	...	Cat _{1,n}
<i>Final properties (SP_n)</i>					
XS [% wt/wt]	3,4	0,5	5,0	...	3,1
MI [g·(10 min) ⁻¹]	7,5	7,5	18,0	...	15,0