

# Modeling, Control and Inversion of Multi-Phase Equilibrium Reactor Systems

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**Abstract:** We propose a simplified modeling approach for multi-phase reactor systems. The model can be used to determine system characteristics, explore parameter sensitivity and test control strategies. The model is based on the thermodynamic equilibrium assumption and invariant inventories to make it computationally inexpensive. We show that the control approach based on the overall inventories of the system can be effectively used for improved performance of such reactor systems. A multi-phase reactor system - the vapor recovery reactor used in carbothermic aluminum reduction process is considered to demonstrate the efficacy of the proposed modeling and control approach.

*Keywords:* Multi-Phase Reactors, Reduced Order Modeling, Inventory Control, Invariants, Thermodynamic Equilibrium.

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## 1. INTRODUCTION

Multi-phase reactor systems are used in a wide range of applications such as in power plants, petrochemical and chemical industries and in various other fields (Dudukovic et al. (1999)). The multi-phase technology is gaining attention because of their variability and ability to perform reaction and separation in one process. In order to quantify the performance and optimize these reactor systems in the absence of any appropriate experimental technique to measure a specified parameter in the multi-phase region or for any expensive/harmful experiments, computational modeling is the key.

Multi-phase reactor systems are difficult to model or to be visualized because of complex phenomena like phase change, significant variation in physical properties and chemical reaction interactions. Also, the characteristics of such systems rely mostly on different processes at different scales. Hence, a consolidated analysis of all the processes at different scales and at different phases is not straightforward and can be of major challenge. Low order models are often employed to help in process development, scale-up, validation and process control.

Multi-phase systems are often modeled based on isothermal assumption with either a pseudo-homogeneous (Kheshgi et al. (1992)) or a heterogeneous model (Hekmat and Vortmeyer (1994)) along with plug flow for gas and liquid phases. There are other studies (Rajashekhar et al. (1998)) where the non-isothermal behavior is modeled by implementing a one-dimensional pseudo-homogeneous energy balance. There are other simplified approaches and a

detailed review of these approaches can be found elsewhere (Dudukovic et al. (1999)).

Khadilkar et al. (1999) developed a model for unsteady-state operation that captures the effect of multi-component transport, multiple reactions, phase change, intra-reactor wet-dry transition. Pellengrini et al. (2008) modeled a hydrocracking Fischer Tropsch unit based on vapor-liquid equilibrium. Jarunghammachote and Dutta (2008) used Gibbs energy minimization method to predict the composition of the gas produced by gasifying a solid fuel in a spouted bed. As a continuation of these studies, we propose a modeling framework for a multi-phase reactor system with a case study leading to modeling and control of a gas-liquid-solid system.

The objective is to develop a model for multi-phase reactor systems which has high accuracy, is computationally cheap such that sensitivity, optimization and control studies can be performed. The modeling approach is based on thermodynamic and reaction equilibrium as it helps in studying the phase behavior and other important properties at the reaction conditions subject to nonideality of reaction mixtures. Further, in order to obtain a reduced order model, we represent the reactor systems based on invariant inventories. This type of modeling helps in employing an inventory based control as the dynamics involved are relatively smooth and can be controlled effectively with traditional control algorithms.

We choose inventories like total mass or total energy to represent the state space of the system (Farschman et al. (1998), Arendsen and Versteeg (2009)). More specifically we use invariant inventories like energy and element mass as they provide minimal state space representation of an equilibrium system. We show that a non-equilibrium multi-phase reactor can be modeled as a network of

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equilibrium stages interconnected by material and energy flows. This method allows to use the structure of physical processes for modeling. The differential equations thus formed have a simple and rather fixed structure. This also separates the model into thermodynamics (algebraic equations) and transport (differential equations) modules, allowing the use of special solution methods for each module according to their own merits.

The passivity based inventory control of nonlinear systems was developed by Ydstie and Viswanath (1994) and applied to transport reaction systems by Ruszkowski et al. (2005). Inventory control has been successfully applied to industrial systems such as float-glass manufacturing process (Ydstie and Jiao (2004), particulate systems (Duenas et al. (2008)) and power plant models (Chengtao and Ydstie (2008)).

In the following sections, we discuss the modeling concept based on invariant inventories and the thermodynamic equilibrium calculations. Then, the dynamic reactor model for a multi-phase system is presented followed by the control concept. Subsequently, we demonstrate the workability of the proposed approach through an industrial multi-phase reactor - vapor recovery reactor used in carbothermic aluminum production.

## 2. MODELING CONCEPT

### 2.1 Process Invariants

Let us consider a high-dimensional networked system represented as

$$\dot{x} = f(x) + g(d, x, u), y = h(x) \quad (1)$$

where  $x$  is the state,  $u$  the control variable,  $d$  the disturbance and  $y$  the measured output. An inventory of the system is defined to be an additive non-negative continuous ( $C^1$ ) function  $\nu : X \rightarrow \mathfrak{R}^+$ . Here  $X$  is the state space. Additivity implies that the inventory of a system is equal to the sum of the inventories of its subsystems.

Using continuity we have the inventory balance from (1)

$$\frac{d\nu(x)}{dt} = p_\nu(x) + \phi_\nu(d, x, u) \quad (2)$$

where

$$p_\nu(x) = \frac{\partial \nu}{\partial x} f(x), \phi_\nu(d, x, u) = \frac{\partial \nu}{\partial x} g(d, x, u)$$

Here  $p_\nu(x)$  represents the drift or the production rate while,  $\phi$  represents the flux from the boundaries. Inventories with  $p_\nu(x) = 0$  are called invariant inventories or simply invariants.

For a chemical process, there exist many invariants. These include mass, energy, momentum and elements or atoms that are neither created nor destroyed. In addition we have so called local invariants which may be molecular species which do not enter in a chemical reaction in the piece of equipment under consideration. Inventories  $E$  are said to be global invariants for a chemical process if  $p_E(x) = 0$  for all  $x \in X$ . The local invariants  $C$  for a process system (1) have  $p_C(x) = 0$  for all  $x \in X_o$ . Here  $X_o \subset X$  a subset is the state space. These local invariants could be the

compounds or functional groups which do not undergo chemical transformation during a specific process. For example during a distillation process to separate methane ( $CH_4$ ) and hydrogen ( $H_2$ ), the compounds  $CH_4$  and  $H_2$  are local invariants since they do not react, while elements  $C$  and  $H$  are global invariants.

In general, we define invariants  $I$  if they satisfy the following

$$p_I(x) = 0 \quad \text{for all } x \in X_o \quad (3)$$

Here,  $X_o \subseteq X$  is the subspace for which (3) holds i.e.  $X_o = \{x : p(x) = 0 \text{ for } x \in X\}$  in the process.

### 2.2 The Equilibrium Assumption

By equilibrium systems we refer to a system that operate under thermodynamic equilibrium and are not limited by kinetics of mass transfer or reaction. There are many examples of equilibrium systems in chemical industry especially in metallurgical industry as they operate at high temperature and large residence times. Many non-equilibrium systems can be modeled as a network of equilibrium systems where we introduce the hypothesis of local equilibrium. The process dynamics of equilibrium systems is only determined by the flow at the boundaries. For kinetically controlled systems, the state of the process with one or more limiting reactions can be written as

$$Z = (U, V, I, \xi) \quad (4)$$

where  $\xi$  is the percentage conversion of each reaction that is kinetically controlled or not at equilibrium. We postulate that the minimal state  $Z$  of an equilibrium process system is defined by the vector of invariant inventories

$$Z = (U, V, I) \quad (5)$$

where  $U$  is the internal energy,  $V$  the volume and  $I$  the moles of invariants present in the system. In a single component system,  $I$  can correspond to the total mass. The intensive variables are

$$w = (1/T, P/T, -\mu/T) \quad (6)$$

where  $T$  is the temperature,  $P$  the pressure and  $\mu$  the chemical potential. In the multi-component system,  $I$  represents a vector of masses or moles of the invariants needed to describe the state. Thus the states of a high dimensional model (1) is projected using invariants onto the low dimensional manifold using the hypothesis of local equilibrium.

$$\frac{dZ}{dt} = \phi(y, d, u), y = h(Z) \quad (7)$$

The net transport  $\phi(y, d, u)$  denotes the flows of mass, energy and volume. The outputs  $y$  are intensive variables, e.g. chemical potentials, temperature and pressure. The function  $h(Z)$  is the mapping of the invariant states  $Z$  to the output or measured variables  $y$ . One form of the function  $h(Z)$  could be the Gibbs free energy minimization that maps the extensive variables like the invariant inventories to the intensive variables. This mapping can be used since the system is under thermodynamic equilibrium and its free energy is minimum. Constitutive equations are used to capture the transport phenomena rather than using the momentum balance equation. Fig. 1 illustrates the idea. The theoretical basis of the proposed modeling approach can be obtained from Aggarwal (2009).

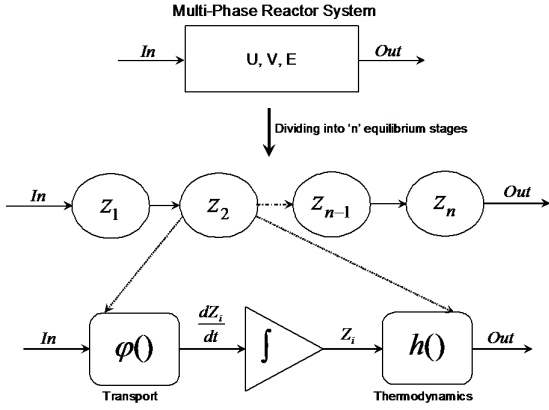


Fig. 1. Multi-phase reactor model based on invariant inventories and thermodynamic equilibrium

### 3. DYNAMIC REACTOR MODEL

Networked representations are developed by tessellating the state space. We now develop a model for a multi-phase reactor systems using the framework shown in Fig. 1. We divide the multi-phase reactor system into  $n$  equilibrium stages. Each stage is assumed to have homogeneous mixing across all phases. The state  $Z$  for a single stage is defined as

$$Z = (U, V, E_i) \quad (8)$$

Here,  $U$  is the internal energy,  $V$  the volume and  $E_i$  the total moles of element  $i$ . Using this definition of state the inventory balance equation (7) for a single stage of the system assuming constant volume can be written as.

$$\frac{dU}{dt} = \sum_{j=1}^{N_c} \Delta(h_j F_j) \quad (9)$$

$$\frac{dV}{dt} = 0$$

$$\frac{dE_i}{dt} = \sum_{j=1}^{N_c} e_{ij} \Delta(F_j)$$

$$\text{where, } \Delta(x) = x^{\text{inflow}} - x^{\text{outflow}} \quad (10)$$

Here,  $N_c$  is the number of compounds present,  $F_j$  and  $h_j$  the molar flow and molar enthalpy of compound  $j$  respectively and  $e_{ij}$  the number of atoms of element  $i$  in compound  $j$ .

The output  $y$  is defined as a vector of intensive variables

$$y = (T, P, C_j) \quad (11)$$

Here,  $T$  is the temperature,  $P$  the pressure and  $C_j$  the concentration of compound  $j$ . The function  $h(Z)$  that maps the state  $Z$  to output  $y$  is defined by Gibbs free energy minimization.

$$(T, P, C_j) = Eq(U, V, E_i) \quad (12)$$

We have used phase subscript to distinguish between elements and compounds. It can be noted that the three matrices are related by the following relation

$$E_i = e_{ij} C_j \quad (13)$$

The constitutive relations for transport are given by

$$F_j = v^\alpha A C_{\alpha j} - D_{\alpha j} A \nabla C_{\alpha j} \quad (14)$$

Here,  $v^\alpha$  is the superficial velocity of phase  $\alpha$ ,  $A$  the cross-sectional area,  $D_{\alpha j}$  the diffusion coefficient of compound  $j$  in phase  $\alpha$  and  $\nabla C_{\alpha j}$  the gradient of compound concentration between stages. Equations (9), (12) and (14) together represent the multi-phase reactor system. Equation (12) calls the thermodynamic database and Gibbs free energy minimization and replaces the kinetics of the conventional modeling methods. Such a methodology is useful for multi-phase systems where the kinetics involved are fast relative to mass or energy transport.

The calculation of constrained equilibria by Gibbs free energy minimization can be formulated as follows (Koukkari and Pajarre (2006)):

$$\min(C^\alpha, x_j^\alpha, T, P) \quad G = \sum_{\alpha} C^\alpha \sum_j \mu_j x_j^\alpha$$

s.t. Chemical equilibrium constraints:

$$\mu_j = \sum_i e_{ij} \lambda_i$$

$$\mu_j = \mu_j^{\text{std}}(T) \quad \text{for solid phase}$$

$$\mu_j = \mu_j^{\text{std}}(T) + RT \ln \gamma_j x_j \quad \text{for liquid phase}$$

$$\mu_j = \mu_j^{\text{std}}(T) + RT \ln P x_j \quad \text{for gas phase}$$

Elemental mass balance constraints:

$$b_i = \sum_{\alpha} C^\alpha \sum_j e_{ij} x_j^\alpha, \quad \sum_j x_j^\alpha = 1$$

Heat balance constraints:

$$U = \sum_{\alpha} C^\alpha \sum_j H_j^\alpha x_j^\alpha$$

Volume balance constraints:

$$V = \sum_{\alpha} C^\alpha \sum_j \rho_j^\alpha x_j^\alpha$$

The computational speed of the equilibrium calculations can be improved by making assumptions related to equilibrium conditions like phases present, temperature ranges etc. Commercial softwares like FACTSAGE available for Gibbs free minimization calculations for metallurgical processes.

### 4. STABLE INVERSION USING INVENTORY CONTROL

In many scale-up, process design and optimization problems it is of interest to invert the process. In such cases, it is necessary to find the flow parameters which give specific states rather than finding the states which correspond to a given flow scenario. In this section we show how inversion can be achieved using inventory control (White et al. (2006)). A control strategy which ensures that an inventory asymptotically tracks a desired set point is called inventory control. Inventory control provides a systematic method of choosing input-output pairs (Alonso and Ydstie (1996, 2001), Ydstie and Alonso (1997)). It controls process inventories  $\nu$  to their set points  $\nu^*$  by choosing the manipulated input variables so that the candidate Lyapunov function decreases. In Farschman et al. (1998) it was shown that the mapping

$$(\phi + p)^T \rightarrow (\nu - \nu^*) \quad (15)$$

is passive with storage function

$$\Psi = \frac{1}{2}(\nu - \nu^*)(\nu - \nu^*) \quad (16)$$

The main limitation of invariant control is that it is practically difficult to measure the inventory of a process although it can be predicted using the intensive variable measurements and the inventory based model. The advantage of inventory control is that it is based on the unique minimum state representation. Hence invertibility and minimum phase conditions should be satisfied. To stabilize the system as represented in (2), Farschman et al. (1998) implemented a Proportional Feedback-Feedforward control like

$$\phi(d, y, u) = -p(x) - K_c(\nu - \nu^*) + \dot{\nu}^* \quad (17)$$

where  $K_c$  is the controller gain. Inventory control is most useful for invariant inventories or the term  $p$  is absent since the modeling requirements are minimal. We refer to the inventory control using invariants as “invariant control”. In such cases, (17) can be written as

$$\phi(d, y, u) = -K_c(\nu - \nu^*) + \dot{\nu}^* \quad (18)$$

The approach is quite general provided  $\phi(d, y, u)$  is invertible with respect to  $u$  and the zero dynamics are stable i.e. convergence of inventories  $\nu$  should also imply convergence of higher order states  $x$ . These problems are more commonly known as input multiplicity and nonminimum phase behavior in control language (Kuhlmann and Bogle (1997)).

The modeling approach can be used to control other intensive variables of interest based on the concept of cascade control (Aggarwal (2009)). The concept is to apply invariant control with a dynamic set point, where the set point of the invariant is varied such that the actual controlled variable follows its set point. For example, if energy is the controlled invariant and temperature is the actual variable to be controlled, then we apply invariant control on the energy while the set point of the energy invariant is varied by  $\dot{U}^* = -K_T(T - T^*)$ .

## 5. CASE STUDY: MODELING AND CONTROL OF THE VAPOR RECOVERY REACTOR USED IN CARBOTHERMIC ALUMINUM PRODUCTION

The Carbothermic process is based on a high-temperature reduction reaction occurring between aluminum oxide and carbon. The components at high temperature react to form molten aluminum and CO gas. Due to high temperatures in the process ( $\sim 2273$  K), large amounts of aluminum and aluminum sub-oxide gases are formed and a significant amount of aluminum is lost. For the process to be energy efficient and economically viable, it is necessary to recover the aluminum in these gases. It is preferable to regain the vapors as aluminum carbide which can be fed into the smelter stage (Garcia-Osorio and Ydstie (2004)). To achieve this, it is proposed to include a Vapor Recovery Reactor (VRR) in the process.

The VRR (Fig. 2) consists of a moving bed of carbon particles into which a continuous stream of off gases (aluminum, aluminum sub-oxide and carbon monoxide) is fed from the main reactor. The gases enter at the bottom of the column at 2100 (K) approximately. They move up the column while reacting with the carbon and forming aluminum carbide. The main chemical reactions taking place are:

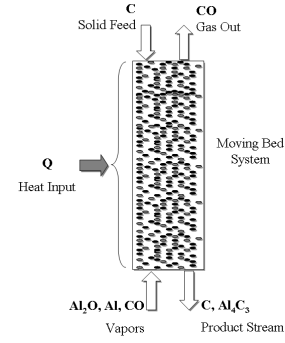
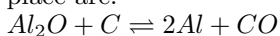
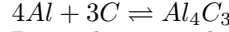
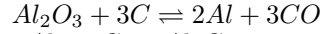


Fig. 2. Vapor Recovery Reactor (VRR)



Depending on the composition and temperature, oxy-carbide slag containing mixture of aluminum oxide and carbide in liquid phase could also form. The slag formation complicates the dynamics of the reactions as there are gas-solid, liquid-solid and gas-liquid reactions taking place in the reactor.

The conventional methods of modeling a reactor require the kinetics of the chemical reactions to be explicitly stated. However, there is little kinetic data available for VRR. However, there has been extensive studies on the thermodynamic properties of the compounds involved.

We assume that VRR is operating under complete thermodynamic equilibrium. This assumption implies that at any spatial point in the VRR, there is instantaneous thermal and chemical equilibrium across all phases present. This assumption is based on the argument that due to high operating temperatures, the chemical reactions are very fast and reach equilibrium almost instantaneously. Previous studies (Fruehan et al. (2002), Garcia-Osorio and Ydstie (2004)) have shown that there can be mass transfer resistance due to diffusion of gases to the solid surface. This would prevent the VRR from operating under equilibrium. These resistances can be included by implementing a population balance model to capture the reaction kinetics (White et al. (2006), Balaji et al. (2009)).

A high dimensional dynamic model of VRR can be obtained from Garcia-Osorio and Ydstie (2004). A low dimensional dynamic model of VRR was simulated by dividing the reactor system into  $n$  equilibrium stages (see Fig. 1). It is assumed that each equilibrium stage is operating isothermally.

$$\frac{dE_i}{dt} = \sum_{j=1}^{N_c} e_{ij} \Delta F_j \quad (19)$$

$$F_j = v^\alpha AC_{\alpha j}$$

$$C_j = Eq(T, P, E_i)$$

For the present work we have developed our own equilibrium module as it can be easily and efficiently integrated with other modules of heat and mass transfer. The minimization is performed by calculating the total Gibbs free energy for every phase combination possible. The feasible phase combination with minimum free energy then gives the global minima. For the given combination of compounds and assumptions there were five 3-phase and

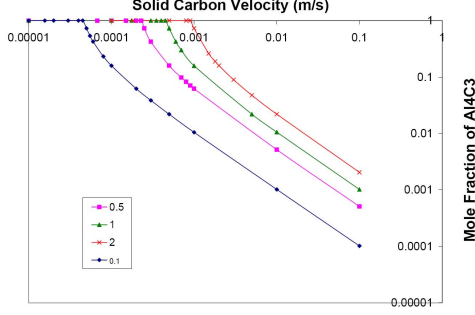


Fig. 3. Simulation results of dynamic VRR model in MATLAB/Simulink

four 2-phase cases possible. The data for standard chemical potentials and activity coefficients was taken from FACT databases (Pelton and Degterov (1999)). The results from our routine were found to be in good agreement with FACTSAGE.

## 6. SIMULATION RESULTS

We performed dynamic simulations of VRR for various input values of solid and gas velocities. For each run we measured the output mole fraction of carbide in the solid outlet when the system reaches a steady state. The carbide mole fractions in the solid outlet as a function of the solid velocity for different gas velocities is shown in Fig. 3.

It can be observed that for a given gas velocity ( $v^{gas}$ ), the carbide  $Al_4C_{3s}$  output increases with decreasing solid velocity ( $v^{solid}$ ) and reaches a constant value of 1 below a certain point. This is because for a given gas velocity, the amount of aluminum to be recovered is fixed. So as we decrease the amount of carbon feed by decreasing the solid velocity, the percentage conversion of carbon to increases till the point when all the carbon is converted into carbide and the mole fraction of carbide at the exit is 1.

On the other hand, if we increase the gas velocity, the amount of aluminum to be recovered from gases increases and hence the mole fraction of carbide in the solid outlet increases. Also the threshold solid velocity for which the outlet fraction becomes 1 increases with increasing gas velocity.

### 6.1 Comparison with Design Relation

To test the validity of the simulations we compared the result with the design relation obtained from overall mass balances of the VRR. The design relation is given as:

$$x_{Al_4C_{3s}}^{out} = \frac{\frac{1}{4}(\gamma C_{Al_g}^{in} + 2\gamma C_{Al_2O_g}^{in})}{\left(\frac{v^{solid}}{v^{gas}}\right) C_{C_s}^{in} - \frac{1}{2}\gamma C_{Al_g}^{in} - 2\gamma C_{Al_2O_g}^{in}} \quad (20)$$

The carbide mole fractions in the solid outlet calculated by the dynamic simulations and the design relation are compared in Fig. 4. It can be observed that the simulation and design relation curves overlap each other. This verifies that the proposed model predicts the outlet compositions accurately.

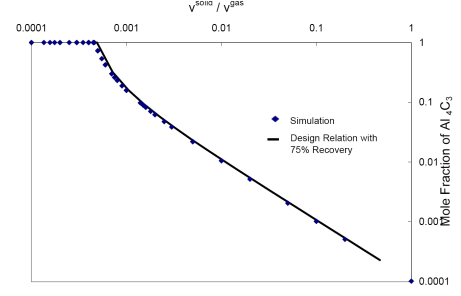


Fig. 4. Comparison of design relation with simulation results

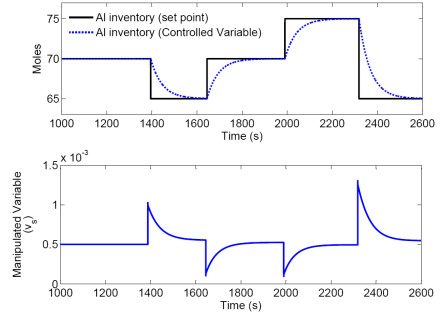


Fig. 5. Control of invariants for VRR (controlled variable, set point and manipulated variable)

### 6.2 Control of Invariants for VRR

The concept of invariant control is applied to VRR dynamic model in MATLAB/Simulink. The objective of the controller is to maintain a desired level of output mole fraction  $x_{Al_4C_{3s}}^{out}$  by manipulating the feed rate of solid carbon i.e.  $v^{solid}$ . The inlet gas composition and the flow rate are determined by the main reactor in the process and is considered as a disturbance variable.

We apply invariant control to achieve this objective. There are 3 invariants in the system i.e.  $E_{Al}$ ,  $E_C$  and  $E_O$ . We choose moles of aluminum  $E_{Al}$  as the controlled invariant. Based on experience and previous process data, the set point of  $Al$  inventory required to achieve a desired level of output mole fraction  $x_{Al_4C_{3s}}^{out}$  can be calculated. If the set point of the actual controlled variable is known, then the set point for the chosen invariant can be calculated. In this study, we assume that the set point of the  $Al$  inventory is known. From (18), the control law can be written as

$$\phi_{Al} = -K_c(E_{Al} - E_{Al}^*) \quad (21)$$

The net flux of  $Al$  into the reactor can be expressed in terms of flux of compounds like

$$\phi_{Al} = \Delta(F_{Al_g} + 2F_{Al_2O_g}) - 4F_{Al_4C_{3s}}^{out} \quad (22)$$

Using the expression for flow in (18) we get the following control law for  $v^{solid}$

$$v^{solid} = \frac{-K_c(E_{Al} - E_{Al}^*) - \Delta(F_{Al_g} + 2F_{Al_2O_g})}{4AC_{Al_4C_{3s}}^{out}} \quad (23)$$

Fig. 5 shows the results of the controller performance. The plot shows the variation in  $Al$  inventory with a set point change. The manipulated variable is also shown in the figure. Fig. 6 shows the actual output variable  $x_{Al_4C_{3s}}^{out}$ . From the results obtained, we can see that the dynamics is

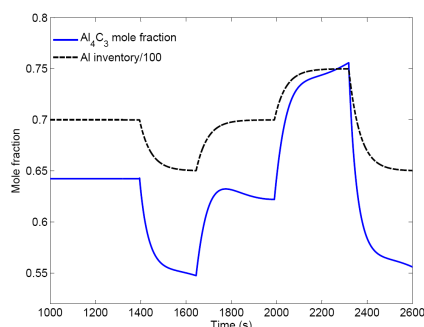


Fig. 6. Control of invariants for VRR (the actual controlled variable and the inventory based controlled variable)

relatively smooth and the controller is stable. By controlling the invariant inventories, the actual controlled variable - the percentage conversion is controlled effectively. The dynamics of  $x_{Al_4C_3s}^{out}$  are slower than that of  $Al$  inventory and hence it takes longer time to reach steady state.

Thus, by exploiting the thermodynamic equilibrium and the invariant inventories of the system, a relatively simple model can be developed and at the same time a stable and effective control can be implemented. In the future works, we plan to compare and analyze the control results of the proposed approach with other conventional methods.

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