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# Identification of the Relationship between Operating Conditions and Polymer Qualities in a Continuous Polymerization Reactor

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## Abstract

A mathematical model is developed to describe the relationship between the manipulated variables (*e.g.* jacket inlet temperature and feed flow rate) and the important qualities (*e.g.* conversion and weight average molecular weight (*Mw*)) in a continuous polymerization reactor. The subspace-based identification method for Wiener model is used to retrieve from the discrete sample data the accurate information about both the structure and initial parameter estimates for iterative parameter optimization methods. The comparison of the output of the identified Wiener model with the outputs of a non-linear plant model shows a fairly satisfactory degree of accordance.

## Introduction

The design of control system frequently requires the accurate model describing the nonlinear dynamics. Such models range from general functional series-based models to models obtained from linear system identification utilizing the Hammerstein model [12,13].

A Wiener system is given by the cascade interconnection of a linear time-invariant system with a static nonlinearity and is particularly useful in representing nonlinearities of a process without introducing the complications associated with general nonlinear operators. This model corresponds to a process with linear dynamics but a nonlinear gain, and can adequately represent many of the nonlinearities commonly encountered in industrial processes such as distillation and pH neutralization [6]. Recently, Verheagen (1998) applied the Wiener model to identification of the temperature-product quality relation in a multi-component distillation column and devised more attractive computational scheme, *e.g.*, having lower computational complexity and higher accuracy [8].

The identification problem for the Wiener model can be formulated as follows : given input/output data sequences, find consistent estimates of the linear part of the model and of the nonlinear mapping. In the literature, the problem of Wiener model identification has been mostly analyzed in the prediction error framework [12,13].

More recently, however, Westwick and Verhaegen [11] proposed subspace based approach making use of the PI MOESP (Past Input MIMO Output-Error State Space) method for the estimation of the system matrices of the linear part ; the PI MOSEP method is the one of subspace-based state space system identification (4SID) methods which have been recently developed and attracted an increasing attention [9,10]. Among the main advantages of such methods we mention the ability to deal with MIMO identification in a straightforward way and the ease for the non-specialist to use due to the small number of parameters which have to be chosen by the user. Also, unlike the case of prediction error methods (PEMs), 4SID algorithms do not require non-linear iterations in the parameter space but are based on computational tools such as the QR factorization and the singular value decomposition (SVD), which make them intrinsically robust from a numerical point of view. Finally, the subspace-based state-space system identification method provides an accurate state-space model for multivariable linear system directly from the input-output data. On the basis of these results, we obtain the model structure and the initial parameter estimates of the Wiener model [4].

In general, the modeling and control of polymerization reactors are difficult tasks for several reasons. First, these reactors often exhibit highly interactive nonlinear dynamic behavior. For example the existence of steady-state multiplicities, parametric sensitivity, and limit cycles for the free-radical polymerization in a continuous stirred-tank reactors (CSTRs) has been shown theoretically and experimentally by Schmidt *et al.* [7]. A second challenge is that the first-principles model for a polymerization reactor may contain a large number of kinetic parameters. Because obtaining these parameters from lab scale test and pilot-plant work can be a very time-consuming endeavor and in addition, there may be processes for which a full understanding of the kinetic mechanism is not available, it may be advantageous to use a model structure whose parameters may be identified

from input-output data [5].

### Continuous Polymerization Reactor Model

Here, we consider a continuous solution polymerization reactor system of methlymethacrylate (MMA) using benzoylperoxide (BPO) as the initiator and ethlyacetate (EA) as the solvent. The reaction kinetics are assumed to follow the free-radical polymerization mechanism including chain-transfer reactions to both solvent and monomer. The free-radical polymerization mechanism is summarized in Table 1. The kinetic parameters are determined using the parameter estimation techniques and are listed in Table 2 [1]. The gel effect is taken into account by the empirical correlations for the gel and glass effects proposed by Schmidt and Ray [7]. The detailed correlations and the other physical properties are represented in Ahn *et al.* [2].

We can derive the differential equations from the mass balances of various species in a polymerization reactor [2].

$$\frac{d(IV)}{dt} = q_f I_f - qI - k_d IV \tag{1}$$

$$\frac{d(MV)}{dt} = q_f M_f - qM - 2fk_d IV - (k_p + k_{trm})MG_0V \tag{2}$$

$$\frac{d(SV)}{dt} = q_f S_f - qS - k_{trs}SG_0V \tag{3}$$

$$\frac{d(G_0V)}{dt} = -qG_0 + 2fk_d IV - k_t {G_0}^2 V \tag{4}$$

$$\frac{d(G_1V)}{dt} = -qG_1 + 2fk_d IV + k_p MG_0V - k_t G_0G_1V + (k_{trm}M + k_{trs}S)(G_0 - G_1)V \tag{5}$$

$$\frac{d(G_2V)}{dt} = -qG_2 + 2fk_d IV + k_p M(G_0 + 2G_1)V - k_t G_0G_2V + (k_{trm}M + k_{trs}S)(G_0 - G_2) \tag{6}$$

Table 1 Free-Radical Polymerization Mechanism

| | |
|---|---|
| Initiation | $I \xrightarrow{k_d} 2\varphi\cdot$ |
| | $\varphi\cdot + M \xrightarrow{k_i} R_1\cdot$ |
| Propagation | $R_1\cdot + M \xrightarrow{k_{p1}} R_2\cdot$ |
| | $R_j\cdot + M \xrightarrow{k_{pj}} R_{j+1}\cdot$ |
| Termination by Combination | $R_i\cdot + R_j\cdot \xrightarrow{k_{tc}} P_{i+j}$ |
| Termination by Disproportionation | $R_i\cdot + R_j\cdot \xrightarrow{k_{td}} P_i + P_j$ |
| Chain transfer To monomer | $R_i\cdot + M \xrightarrow{k_{trm}} P_i + R_1\cdot$ |
| Chain transfer To solvent | $R_i\cdot + S \xrightarrow{k_{trs}} P_i + S\cdot$ |

Table 2 Rate Constants used in the Model for MMA Polymerization

| Rate Constants | Expression |
|---|---|
| $k_d[s^{-1}]$ | $1.25\times10^{18}\exp(-35473/RT)$ |
| $k_{p0}$[l/mol/s] | $2.94\times10^{6}\exp(-5656/RT)$ |
| $k_{t0}$[l/mol/s] | $5.20\times10^{8}\exp(-1394/RT)$ |
| $k_{td0}/k_{t0}$ | $1.83\times10^{27}\exp(-44467/RT)$ |
| $k_{trm}$[l/mol/s] | $9.32\times10^{4}\exp(-13971/RT)$ |
| $k_{trs}$[l/mol/s] | $8.79\times10^{-5}\exp(-42.6/RT)$ |

*R : Ideal gas constant*

$$\frac{d(F_0V)}{dt} = -qF_0 + \frac{1}{2}(k_t + k_{td}){G_0}^2V + k_{trm}MG_0V + k_{trs}SG_0V \tag{7}$$

$$\frac{d(F_1V)}{dt} = -qF_1 + k_t G_0G_1V + (k_{trm}M + k_{trs}S)G_1V \tag{8}$$

$$\frac{d(F_2V)}{dt} = -qF_2 + k_{tc}(G_0G_2 + {G_1}^2)V + k_{td}G_0G_2V + (k_{trm}M + k_{trs}S)G_2 \tag{9}$$

where $I$, $M$, and $S$ represent the concentrations of initiator, monomer and solvent, respectively, and subscript $f$ denotes the feed condition. Also $q_f$ is the feed flow rate and $q$ is the overflow rate which makes the reactor level constant. The symbol $f$ indicates the initiator efficiency. In addition, $G_k$ and $F_k$ denotes the $k$-th moments of living and dead polymer concentrations, respectively, and are defined as follows :

$$G_k = \sum_{n=1}^{\infty} n^k R_n(t), \quad k = 0, 1, 2 \tag{10}$$

$$F_k = \sum_{n=1}^{\infty} n^k P_n(t), \quad k = 0, 1, 2 \tag{11}$$

Once the $G_k$ and $F_k$ are known, the weight average molecular weight ($Mw$) can be determined by the following formula :

$$Mw = Mm \times \frac{(G_2 + F_2)}{(G_1 + F_1)} \tag{12}$$

where $Mm$ is the molecular weight of monomer.

We also consider the energy balances for reactor and jacket, and use the equations for the volume change of the reaction mixture to calculate $q$ [1].

### Application of the Systematic Procedure to Identify Wiener System

**Wiener System Identification Problem**

We shall assume that the system to be identified may be described by the following Linear Time-Invariant (LTI) state space model :

$$\begin{aligned} x_{k+1} &= Ax_k + Bu_{k-d} \\ y_{k+1} &= Cx_k + Du_{k-d} \end{aligned} \qquad (13)$$

where $x_k \in R^n$ is the state vector, $u_k \in R^m$ is the input vector, $y_k \in R^l$ is the output vector and $d$ is the dead-time.

The measurement equation of the output is given by the expression :

$$z_k = f(x_k) + v_k \qquad (14)$$

where $z_k \in R^l$ is the observed output, $f(\cdot): R^l \to R^l$ is a non-linear vector function and $v_k$ is a zero-mean stochastic process of arbitrary color.

The Wiener system identification problem is now stated as :

Let the following data sequence of input/output ($i/o$) data for the system (13-14) be given by

$$\begin{bmatrix} u_j & u_{j+1} & \cdots & u_{j+N-1} \\ z_j & z_{j+1} & \cdots & z_{j+N-1} \end{bmatrix} \qquad (15)$$

and assume that the input sequence $\{u_k\}$ is sufficiently persistently exciting as defined in Verhaegen (1993) and statistically independent from the perturbation $\{v_k\}$, the task is to find ($a$) the order of and ($b$) a statistically consistent estimate of the LTI state space model and the initial conditions (up to a similarity transformation), and ($c$) the dead-time $d$ as well as ($d$) an estimate of $f(\cdot)$ [8,9,10].

**Data generating from mathematical model**

For the identification of a continuous polymerization rector, we use the input-output data obtained from numerical simulations of the nonlinear model for the continuous polymerization reactor. In general, the most common types of excitation signals used for collection of identification data are step, impulse and Pseudo Random Binary Sequences (PRBS). Step and impulse responses have been used in the development of linear Single-Input/Single-Output (SISO) transfer functions, but these signals are not applicable to Multiple-Input /Multiple-Output (MIMO) identification because they do not adequately excite the process and thus lead to ill-conditioned data matrices. On the other hand, PRBS are well suited for MIMO identification [3].

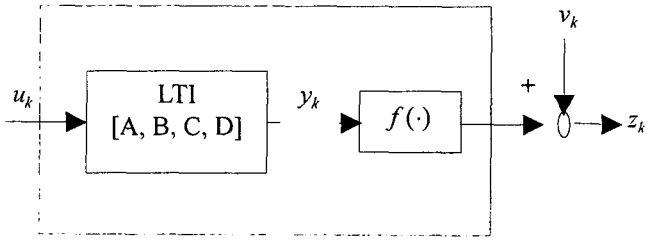


Figure 1. A schematic representation of the Wiener model.

In this study, we use the inlet temperature of the reactor jacket $T_{jin}$ (from 75°C to 80°C) and the feed flow rate $q_f$ (from 5 *ml/min* to 15 *ml/min*) as the test inputs. For the purpose of increasing the accuracy of identified model, 5 sets of PRBS inputs of $T_{jin}$ and $q_f$, respectively, are used for generating $i/o$ data and 5 sets of outputs (conversion and $Mw$) are obtained. In Figure 2, a set of input/output data are shown. In the upper two diagrams of Figure 2, the chance of the signal changing level of PRBS inputs is 0.2. The outputs in the lower two diagrams of Figure 2, start from the steady state values (Conversion = 0.1158, $Mw$ = 169.592) which calculated in advance.

**Structure Selection using PI MOSEP**

Identification is executed with reference to the systematic procedure to identify Wiener system proposed by Verheagen [8]. In order to perform the first step of this strategy in a systematic manner, one needs to evaluate the model accuracy measure for all different combinations of feasible model orders and dead-times. For this purpose we use the Variance Accounted For (VAF) index, which is defined as

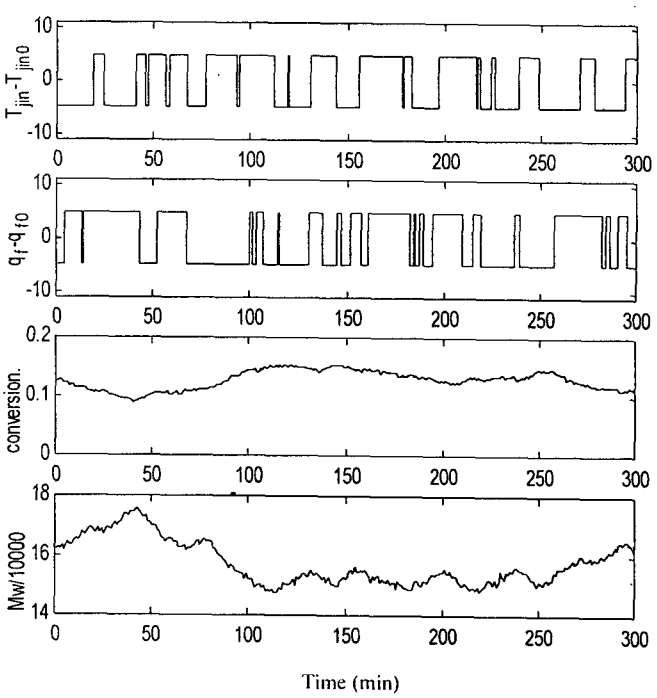


Figure 2. Input/output data from the mathematical model equations.

$$VAF = 100\left(1 - \frac{\sqrt{\sum_{i=1}^{N}(z_i - \hat{z}_i)^2}}{\sqrt{\sum_{i=1}^{N} z_i^2}}\right) \qquad (16)$$

The range of the VAF index is between $-\infty$ and 100%. Instead of this brute force manner, we use subspace identification to get some insight about the order of the underlying system. We first identify the LTI part of the Wiener system, using the PI (Past Input) subspace identification scheme as if the nonlinearities were not present and determine the order of the LTI system and the dead-time. This is attractive when no prior information is available. To get some insight into the order of the system to be identified with subspace identification schemes only (*a*) an overestimate of the order of the system (taken equal to 10) and (*b*) the specification of the dead-time are required (taken equal to 0 minute) [9,10,11].

Since the 5 sets of *i/o* data are used for identification of the system successively, the system order can be estimated more accurately as the number of data set used increases. Singular values obtained by the PI subspace identification scheme are shown in Figure 3. We observe a gap between the second and third singular values, indicating that the underlying system is of order 2. Fixing the order of the LTI system to 2, we can evaluate the VAF for different dead-times in the range between 1 and 4 minutes for input. The result shows that 1 minute yields the best model predictions. Though we could use this information to specify bounds on the dead time in a parametric optimization problem where this is another variable to optimize, we fix the dead time to 1 minute in subsequent calculations. In the lower two diagrams of Figure 4, we show the output of LTI system by PI scheme and the

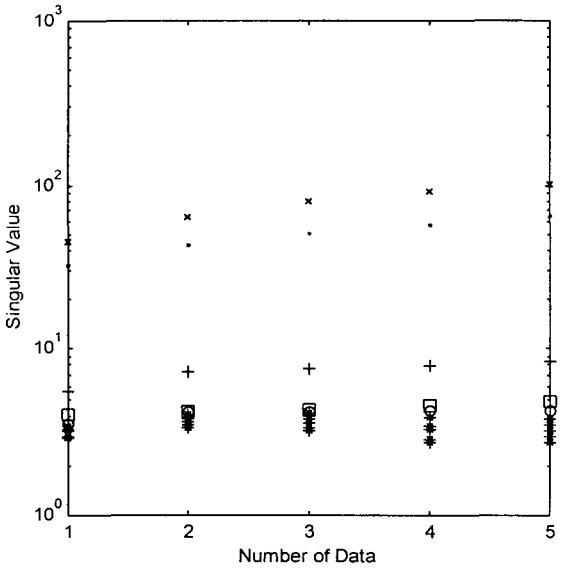


Figure 3. Singular values obtained by using 5 sets of data.

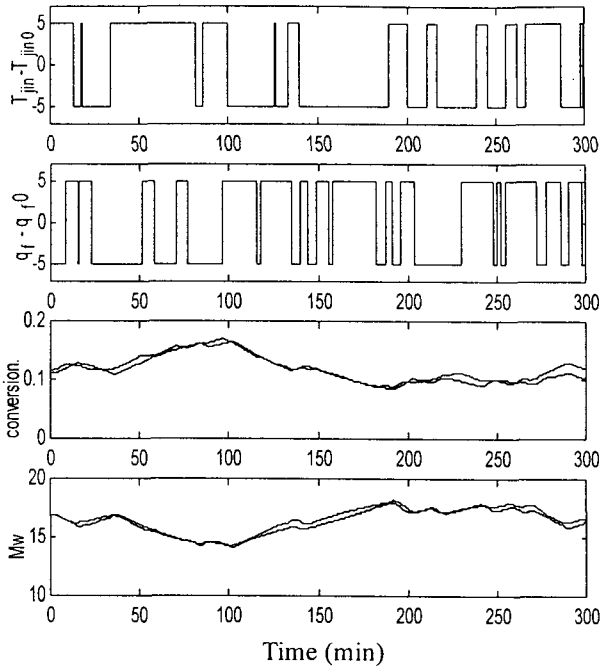


Figure 4. Comparison between the outputs of LTI system and the nonlinear outputs.

output of the nonlinear part of the system. The VAF index of this estimate is 89.7589% and 93.1746 % for conversion and *Mw*, respectively. We plot the computed output of the selected LTI system $\hat{y}_k$ versus the actual nonlinear output in Figure 5. The actual nonlinear conversion, as displayed by the symbol x in this figure, shows a very complicated aspect because it depends on the conversion and *Mw* of LTI system. A MIMO static nonlinear function between the LTI outputs and the measured outputs is estimated on the basis of Tchebychev polynomials as follows :

$$\min_{\gamma_i} \sum_{k=j}^{j+N-1} \left\| z_k - \Phi(\hat{y}_k) \right\| \qquad (17)$$

where Tchebychev polynomials are represented by the expression :

$$\Phi(\hat{y}_k) = \sum_{i=0}^{n_1} \gamma_i \hat{y}^i{}_k = \left[\Phi_1 \quad \Phi_2\right]^T \qquad (18)$$

$$\Phi_1(\hat{y}_k) = \gamma_0 + (\gamma_{1,1}\hat{y}_{k,1} + \gamma_{1,2}\hat{y}_{k,2}) + (\gamma_{2,1}\hat{y}_{k,1}{}^2 + \gamma_{2,2}\hat{y}_{k,2}{}^2) + \cdots + (\gamma_{5,1}\hat{y}_{k,1}{}^{n_1} + \gamma_{5,2}\hat{y}_{k,2}{}^{n_1}) \qquad (19)$$

Before estimating the coefficients of polynomials the input signal of the function is shifted and scaled to fall within the region [-1, 1]. The estimate of the static nonlinearity, depicted by the dotted line in Figure 5, shows a very nonlinear relationship. Since actual conversion correlates with $M_w$ as

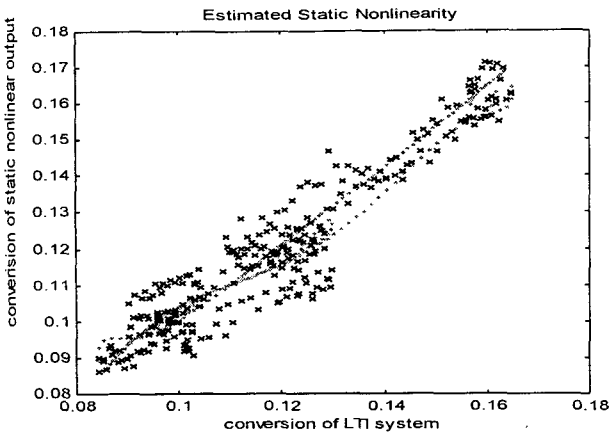


Figure 5. The output of LTI system vs the true and the estimated nonlinear output [conversion]

well as with conversion of LTI system, conversion of LTI system can have more than one corresponding value of actual nonlinear output. The output estimate by MIMO static nonlinear function is plotted in Figure 6. The VAF indices for conversion and *Mw* are 91.2580 % and 93.2750 %, respectively. The VAF indices of this estimate are improved compared to PI MOSEP scheme.

We can summarize from the initial structure selection step that the model to be improved in the subsequent steps of the systematic procedure should be a second order model with dead-time equal to 1 minute with two inputs.

**Model Improvement Using Full Parameter Optimization**

Since the input used for identification is not Gaussian, PI-MOSEP may give biased estimate of the linear part. Therefore, we now need to use a nonlinear optimization technique to find the right model. We parameterize the Wiener system as Eqs. (20) and (21).

$$\hat{x}_{k+1}(a_s) = \begin{bmatrix} -a_1 & 1 & \cdots & 0 \\ -a_2 & 0 & \ddots & 0 \\ \vdots & \vdots & & \vdots \\ -a_{n-1} & 0 & \cdots & 1 \\ -a_n & 0 & \cdots & 0 \end{bmatrix} \hat{x}_k(a_s) + Bu(k) \tag{20}$$

$$\hat{y}_k(a_s) = \begin{bmatrix} I_l & 0 & \cdots & 0 \end{bmatrix} \hat{x}_k(a_s) \tag{21}$$

Let $\theta$ denote the parameters that specify the linear time-invariant system, *i.e.* the parameters $a_s$, those of the matrix B and the initial conditions. If $\hat{y}(\theta)$ represents the predicted output based on the coefficients $\theta$, then we can define the following full parameter optimization problem:

$$\min_{\theta} \min_{\gamma_i} \sum_{k=j}^{j+N-1} \left\| z_k - \sum_{i=0}^{n_1} \gamma_i \hat{y}_k{}^i(\theta) \right\| \tag{22}$$

The principle of separable least squares can reformulate the above optimization problem in terms of $\theta$ only. From the previous step we can specify constraints on the parameter values providing the iterative optimization with good initial estimates. The output of the model that resulted from solving the optimization problem (22) is plotted in Figure 7. The VAF indices are 93.8488 % and 97.7000 %. We observe that the estimation of Wiener system is improved compared to the results of Figure 7. The relationship between the outputs of the linear model and the actual nonlinear outputs is shown in Figure 8. The different scale along the x-axis, compared to Figure 5, and the split nonlinearity are due to the nature in the model description of Wiener model. Now the nature of static nonlinearity is even more transparent.

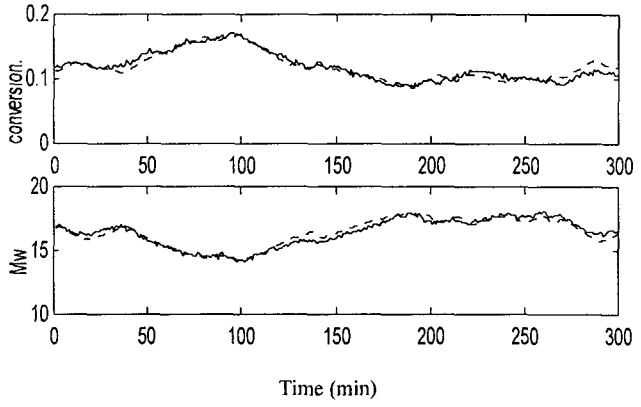


Figure 6. Comparison between the true outputs and the outputs of the identified Wiener model based on only Tchebychev polynomial.

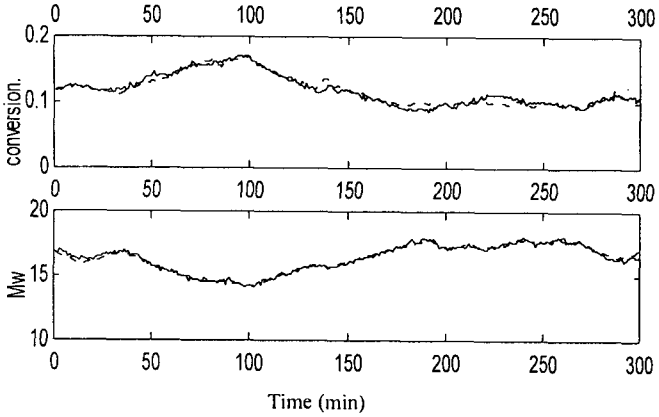


Figure 7. Comparison between the true outputs and the outputs of the identified Wiener model using iterative optimization based on tchebychev polynomial.

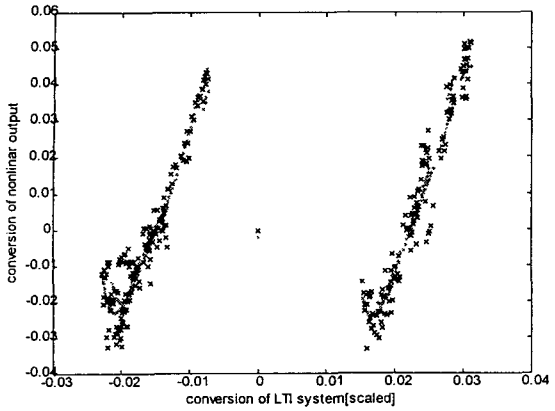


Figure 8. The scaled output of LTI system vs. the true and the estimated nonlinear output using full parameter optimization [conversion].

## Concluding Remarks

In this paper, we applied a systematic procedure to identify MIMO Wiener system to the identification of the relationship between the manipulated variables such as jacket inlet temperature and feed flow rate and the important qualities suc iuous polymerization reactor. The first step of subspace-based Wiener model identification method only requires very little and coarse *a priori* knowledge about the model structure. It is shown that this feature allows the user to confirm and improve his prior knowledge about the model structure and supplies the iterative parameter optimization methods with reliable initial estimates. As the systematic procedure proceeds, the estimation of the model is improved (which is shown in the Table 3). Finally, we could obtain the very accurate MIMO Wiener model without the exhaustive "trial-and-error" search procedure.

Table 3. Comparison of VAF in each systematic step

| Step | VAF(%) | |
|---|---|---|
| | Conversion | $M_w$ |
| PI scheme | 89.7589 | 93.1746 |
| Tchebychev polynomial | 91.2810 | 93.2750 |
| Full parameter optimization | 93.8488 | 97.7000 |


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