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INFERENCE OF CONVERSION AND PURITY FOR ETBE REACTIVE DISTILLATION

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Abstract. *Reactive distillation (RD), an unconventional and attractive technique, has been applied in fuel ether production. A typical application of RD is the synthesis of the widely used methyl tert-butyl ether (MTBE). RD has also been found to have potential to produce high quality ethyl tert-butyl ether (ETBE), a potential alternative to MTBE. A RD process integrates conventional reaction and separation into a single unit, resulting in extra complexity and dual process objectives, i.e. maximization of reactant conversion and purity of products. The conversion and the purity are thus important variables to be controlled in RD of ETBE. Unfortunately, both of them are not economically and reliably available for closed-loop control. This study aims to develop an effective method to infer the conversion and the purity from multiple temperature measurements that are easily available on-line and in real time. Nonlinear inferential models are recommended for ETBE synthesis with a ten-stage pilot scale RD column. The models are two-variable third-order regressive models, in which the temperature measurements of the reboiler and the bottom reactive section are employed. Experimental design, model identification, and model testing are also investigated.*

Keywords: *reactive distillation, inferential model, conversion, purity*

1. INTRODUCTION

Gasoline is the main energy source for most motor vehicles. Its quality directly affects environmental pollution. A significant step to improve the gasoline quality is the removal of lead by adding octane enhancers. Another worldwide trend to further improve the gasoline quality is the introduction of oxygenates to substantially reduce emissions from motor vehicles.

There has been a continuous effort for development and production of high-performance gasoline additives. Methyl *tert*-butyl ether (MTBE) has a dual advantage in lead removal and oxygenate introduction and thus has been widely used as a gasoline additive. However, recent studies have indicated that MTBE has significant water ingress problem that may pollute underground waters and hence cause cancers. Ethyl *tert*-butyl ether (ETBE) has been found to be a potential alternative to MTBE. Although currently ETBE is more expensive than MTBE, it has higher performance, less water contamination, and is produced from renewable products.

Reactive distillation (RD) is an unconventional and attractive technique for syntheses of fuel ethers. It integrates conventional reaction and separation units into a single column. This functional integration results in extra complexity, which is yet to be fully understood. The RD is, thus, exceptionally difficult to operate and control.

On the other hand, the integration of reaction and separation also leads to dual process objectives: maximization of reactant conversion and purity of products. These two objectives

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are usually inconsistent, i.e. they cannot be achieved simultaneously as in the conventional route. A compromise between the conversion and the purity is thus necessary in RD operation, unless the products purity is the priority objective. A high conversion is always expected with a satisfactory purity. This is largely dependent on high-performance closed-loop control for both conversion and purity.

Closed-loop control requires that the measurements of the variable to be controlled are available. Unfortunately, both reactant conversion and products purity cannot be economically and reliably measured in real-time. A method to overcome this difficulty is to indirectly control the conversion and purity by controlling some other variables, which are easily available and are indicators of the conversion and purity. Such indicators are, however, not easy to find due to the unavailability of a one-to-one relationship between a single variable and the conversion or purity. An alternative method to overcome the difficulty is to employ inferential control for both conversion and purity.

In inferential control, the unavailable variables are inferred from multiple measurable variables. A linear inferential model, which employs two temperature variables, has been proposed for conversion by Sneesby, Tadó and Smith (1999). The main difficulty in using linear model is the nonlinearity in the RD process. A similar problem exists in composition estimation for conventional distillation processes (Mejdell and Skogestad, 1991a; 1991b).

Discarding the linear modeling approach, this paper aims to develop nonlinear inferential models for both conversion and purity of ETBE RD. Multiple temperature variables will be employed in the inferential models. A ten-stage pilot scale RD column for ETBE synthesis will be considered, which will be described in detail in the succeeding section.

2. PILOT SCALE RD PROCESS

A pilot scale RD column is shown in Fig. 1. It has a height of 4.1m and a diameter of 0.155m. The RD process consists of a total condenser, a partial reboiler, and three column sections respectively for rectification, reaction and stripping. The condenser and the reboiler are considered as two separate stages, as is usually done. The rectifying, reactive, and stripping sections have one, three, and four stages, respectively. Thus, the RD process has ten stages altogether, which are numbered from top to bottom. The feed is introduced at stage 6.

The column is filled with two novel packings, one of which contains the catalyst (Amberlyst 15TM) necessary for the etherification reaction.

Transmitters are used in the pilot scale RD process to measure temperature, flow rate, pressure, and level variables, as shown in Fig. 1. For temperatures, thermocouples are installed at the reflux pipeline, at the top and bottom of the column, at the top and bottom of reactive section, and at stage 8.

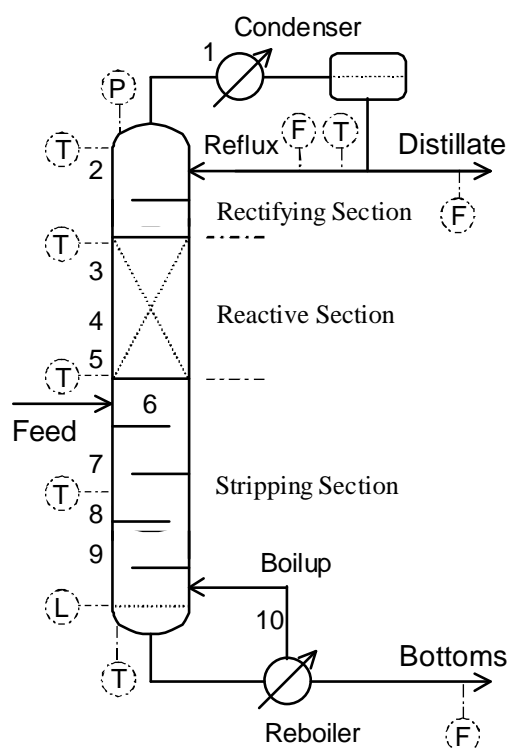
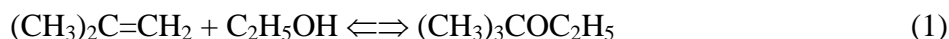


Figure 1. A pilot scale RD column for ETBE synthesis (T, F, P, L: transmitters of temperature, flow rate, pressure, and level variables).

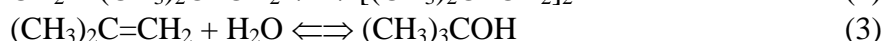
The measured flow rates include reflux, distillate and bottoms flow rates. The column pressure is measured at the top of the column.

The pilot scale RD process is designed for ETBE synthesis from ethanol and a mixed C₄ olefin stream, which contains about 40% isobutylene (typically of a cracking unit product). In ETBE synthesis, the dominant chemical reaction is the exothermic, reversible etherification of ethanol and isobutylene to form ETBE.



This reaction occurs substantially at temperatures below 90°C.

There are two side reactions, the dimerisation of isobutylene to form isobutanol and the hydration of isobutylene to form di-isobutylene:



These side reactions could be neglected in the study of process control due to their minor effects on process dynamics.

The pilot scale RD column is typically operated at the feed temperature of 25°C and the overhead pressure of 950kPa. The overhead pressure is maintained by adjusting the condenser duty. A set of typical operating conditions of the pilot scale RD process is shown in Table 1.

Table 1. A Set of Typical Operating Conditions

Feed composition (%):	ETBE: 29.1; ethanol: 9.1; isobutylene: 7.3; n-butylenes: 54.5 (stoichiometric excess ethanol: 5.0)
Feed temperature	25 °C
Feed rate	0.76 L/min
Distillate rate	0.45 L/min
Reflux rate	2.5 L/min
Bottoms rate	0.485 L/min
Isobutylene conversion	98.24 mol%
Bottoms ether purity	94.03 mol%
Distillate ethanol purity	0.79 mol%
Overhead Pressure	950 kPa
Condenser temperature	74.2 °C
Temperature of top reactive section (stage 3)	75.0 °C
Temperature of bottom reactive section (stage 5)	80.5 °C
Temperature of middle stripping section (stage 8)	134.1 °C
Reboiler temperature	156.4 °C
Reboiler duty	8.36 kW

3. DATA COLLECTION AND PROCESSING

Process data that cover a wide range of operating conditions are necessary in the development of inferential models for conversion and purity. Both simulation data and real plant data can be employed, as discussed by Sneesby *et al.* (1999) for conversion inference. This work is based on simulation data. One of the advantages of using simulation data is that the data are free of measurement noises that may be present in real plant operation, although

model mismatch is inevitable in simulations. Another advantage of using simulation data is that the process data that covers a wide range of operating conditions can be easily obtained because changing operating conditions is easy in simulations.

The quality of simulation data relies on good process models. There are two main types of models for RD processes: equilibrium (EQ) models and non-equilibrium (NEQ) models (rate-based models). All RD processes are certainly rate-based in nature, while most of the available RD process models are EQ-based due to the simplicities in their structures and the difficulties in applications of rate-based models (Higler *et al.* 1998, Pilavachi *et al.* 1997). The rate-based models for RD processes are still in the development stage. The EQ-based process model developed by Sneesby *et al.* (1997a, 1997b) is adopted here. It has been demonstrated to have good performance.

In the simulations of the RD process shown in Fig. 1, the feed temperature is assumed to be 25°C. Through adjusting the condenser duty, the overhead pressure of the column is maintained at 950kPa. Changes are made in reboiler duty from 7.5 to 9.0kW, in reflux rate from 2.0 to 3.0L/min, and in feed rate from 6.2 to 7.4L/min.

As shown in Fig. 1, there are six temperatures available in the RD process. These temperatures are denoted by x with a subscript of the stage number. Condenser temperature, x_1 , and the temperature of the column top, x_2 , are not suitable for inference of conversion and purity as they behave with small variations for a wide range of operating conditions. It may be difficult to distinguish these variations from noise. x_1 and x_2 are, therefore, excluded in the inference of conversion and purity. The other four temperatures (x_3 , x_5 , x_8 , and x_{10}), i.e., the temperatures at the top and bottom of the reactive section, the temperature of stage 8, and the reboiler temperature, are considered as independent variables to infer the conversion and purity. Different combinations of these four temperatures will be studied.

The equation based commercial simulation package SpeedUp Release 5.4 for VMSTM (Aspen Technology, Inc, 1993) is used to simulate the RD process. 54 observations spanning the significant operating range are generated for model identification. These observations are shown in Fig. 2 for conversion and Fig. 3 for purity, respectively. The upper three subplots of Figs. 2 and 3 display all the 54 observations. In the lower subplot of Fig. 2 (or 3), 13 and 18 observations of the total 54 are respectively used to show the relationships of conversion (or purity) versus reflux rate without changes in reboiler duty and conversion (or purity) versus reboiler duty without changes in reflux rate. The simulation results clearly show multiplicity behaviors of the RD process (Jacobs and Krishna, 1993).

In addition to the above mentioned sampling data, 33 more observations are produced for model testing, where reflux ratio, instead of reflux rate, is made changeable from 4.0 to 7.0.

Regression method is employed in development of inferential models for conversion and purity. The model identification and model testing are carried out using the commercial simulation package MATLAB version 5.0, a high-performance tool for numerical computation and visualization (The MathWorks, Inc, 1995).

4. CONVERSION INFERENCE

Selected regression results for conversion inference are shown in Table 2, where the first 5 and last 2 candidates correspond to two- and three-variable models, respectively. For the specific orders, all models shown in Table 2 are optimal except the two-variable models M2 and M3, which are suboptimal. The results will be discussed in detail below.

If conversion inference is limited to be linear and two-variable, both M1 and M2 are good choices with only small differences in correlation coefficients and standard deviations. Let y denote the conversion with the unit of mol%. M1 and M2 are respectively described by

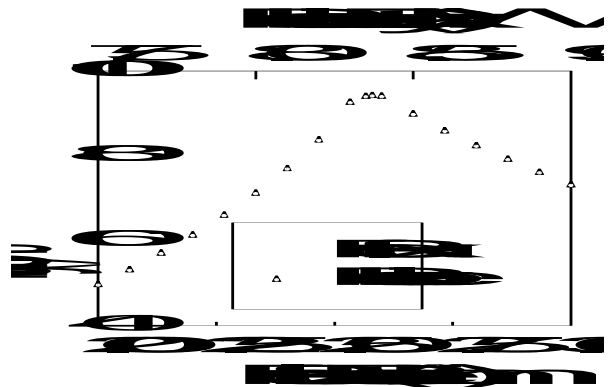
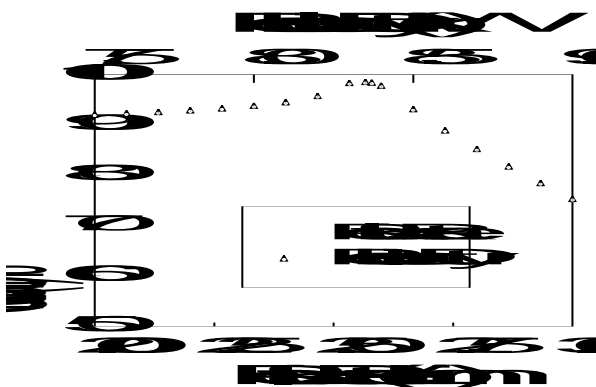
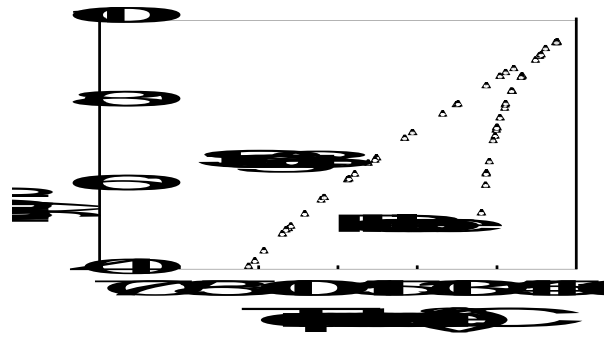
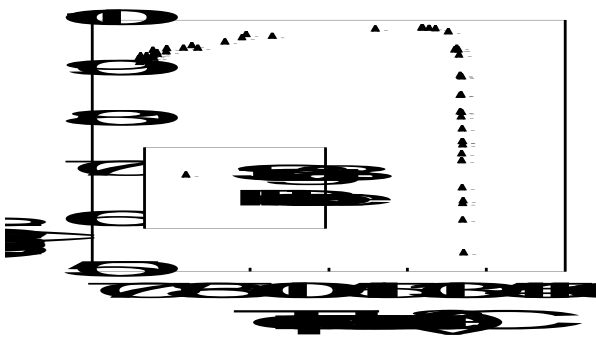
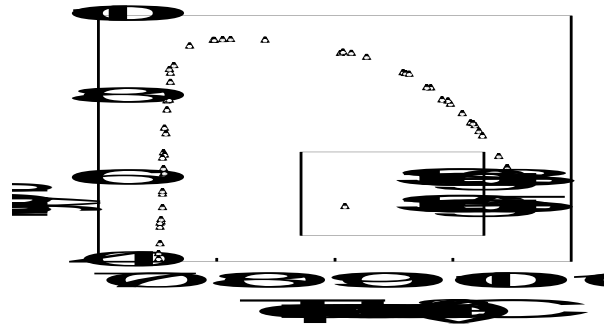
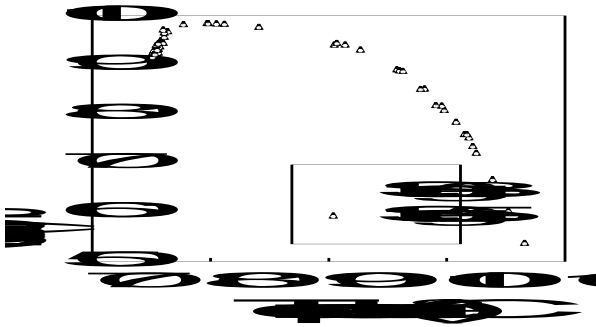
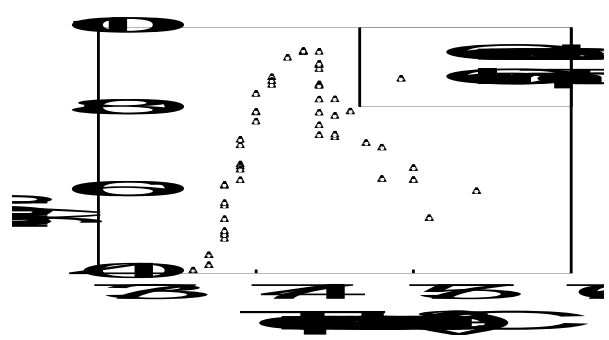
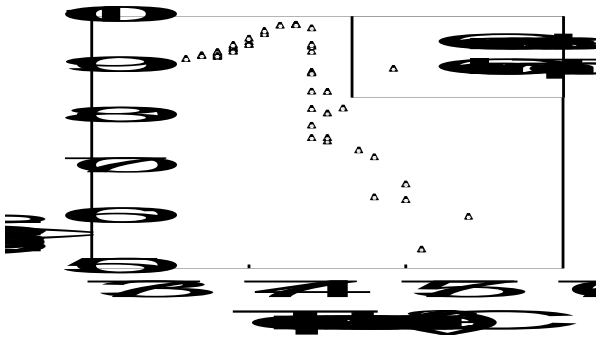


Figure 2. Conversion versus temperatures, reflux rate, and reboiler duty.

Figure 3. Purity versus temperatures, reflux rate, and reboiler duty.

Table 2. Selected Regression Results for Conversion Inference

Models	Variables	Max Orders	Correlation Coefficients		Standard Deviations	
			Fitting	Testing	Fitting	Testing
2-Variable models:						
M1	x_3x_8	1	0.9924	0.9963	1.3516	1.1973
M2	x_3x_{10}	1	0.9904	0.9925	1.5124	1.6558
M3	x_3x_5	2	0.9991	0.9989	0.4773	0.6433
M4	x_5x_8	3	0.9997	0.9994	0.2862	0.4601
M5	x_5x_{10}	3	0.9996	0.9996	0.2996	0.4008
3-Variable models:						
M6	$x_3x_8x_{10}$	1	0.9948	0.9968	1.1140	1.0838
M7	$x_3x_5x_{10}$	2	0.9998	0.9997	0.2427	0.3193

$$\text{M1: } y = -4.3236x_3 + 0.1818x_8 + 398.10 \quad (4)$$

$$\text{M2: } y = -3.6751x_3 + 0.2019x_{10} + 341.68 \quad (5)$$

Taking into account the nominal values of x_3 , x_8 , and x_{10} shown in Table 1, four decimal points are retained in the parameters of linear terms to ensure the resulting precision with two decimal points.

The above two equations imply that an increase of 1°C in x_3 will lead to a decrease of about 4mol% in conversion, while an increase of 1°C in x_8 or x_{10} will result in an increase of about 0.2mol% in conversion. Similar results have also been obtained by Sneesby *et al.* (1999) under different operating conditions.

The inference performance measured by correlation coefficient and standard deviation can be significantly improved if nonlinear terms are introduced. Table 2 shows that all second- and third-order two-variable models, i.e. M3 through M5, outperform the two-variable linear models M1 and M2. The optimal second-order two-variable model, M3, is a combination of two reactive zone temperatures, x_3 and x_5 . M3 is given by

$$\text{M3: } y = 0.295748 x_3^2 + 2.9304x_3 - 0.500666x_3x_5 + 35.3765x_5 + 0.008762 x_5^2 - 1666.85 \quad (6)$$

Considering the nominal values of x_3 and x_5 , different decimal points are retained in different model parameters to ensure the resulting precision with two decimal points. The correlation coefficients of M3 for both fitting and testing reach about 0.9990, compared to 0.9924 for fitting and 0.9963 for testing in M1. The standard deviations are reduced to about half of those in M1.

Introducing third-order terms will further improve the model performance. As shown in Table 2, third-order two-variable models M4 and M5 are superior to the optimal second-order model M3. They give very good performance with the correlation coefficients larger than 0.9994 and the standard deviations less than 0.47. M4 and M5 are respectively described by

$$\begin{aligned} \text{M4: } y = & -0.00453397 x_5^3 + 1.242286 x_5^2 + 89.1038x_5 - 0.00038915 x_5^2 x_8 - 0.375650x_5x_8 \\ & + 0.00189890x_5 x_8^2 + 35.3817x_8 - 0.187182 x_8^2 + 0.00014009 x_8^3 + 1513.91 \end{aligned} \quad (7)$$

$$\begin{aligned} \text{M5: } y = & -0.00466812 x_5^3 + 1.569083 x_5^2 - 216.3114x_5 - 0.00250493 x_5^2 x_{10} + 1.119566x_5x_{10} \\ & - 0.00236918x_5 x_{10}^2 - 62.8709x_{10} + 0.120759 x_{10}^2 + 0.00015479 x_{10}^3 + 9173.63 \end{aligned} \quad (8)$$

Again, different decimal points are retained in different model parameters to ensure the resulting precision with two decimal points. There is only a small performance difference between M4 and M5. M4 employs x_5 and x_8 , while M5 utilizes x_5 and x_{10} . M5 is recommended here for conversion inference because x_{10} is already measured for other reasons.

For both model identification and model testing, the correlation coefficients of the recommended model, M5, are sufficiently high (larger than 0.9996) and the standard deviations of the model are sufficiently small (less than 0.41). Due to inevitable measurement noises that affect model performance, there is no necessity to further increase the model order.

Table 2 also shows the results of three-variable linear and nonlinear inferential models for conversion. Compared with the two-variable linear model, M1, the best three-variable linear model, M6, has only limited performance improvement. A three-variable second-order nonlinear model and a two-variable third-order nonlinear model have the same number of parameters and thus are comparable in complexity. Compared with the recommended M5, the best three-variable second-order nonlinear model, M7, has only limited performance improvement while an extra temperature is required. A three-variable model is, therefore, not recommended for conversion inference.

5. PURITY INFERENCE

Selected regression results for purity inference are shown in Table 3, where the first 3 and the last 2 candidates correspond to two- and three-variable models, respectively. All models in Table 3 are optimal for the specific orders. In the following discussions about purity inferential models, different decimal points are retained for different model parameters to ensure the resulting precision with two decimal points, as in conversion inference.

Table 3. Selected Regression Results for Purity Inference

Models	Variables	Max Orders	Correlation Coefficients		Standard Deviations	
			Fitting	Testing	Fitting	Testing
2-Variable models:						
M8	$x_3 x_{10}$	1	0.9947	0.9847	1.6004	2.1905
M9	$x_3 x_{10}$	2	0.9992	0.9977	0.6363	0.9357
M10	$x_5 x_{10}$	3	0.9999	0.9997	0.1997	0.2961
3-Variable models:						
M11	$x_3 x_5 x_{10}$	1	0.9967	0.9933	1.2682	1.4505
M12	$x_3 x_5 x_{10}$	2	0.9999	0.9996	0.2342	0.3715

As shown in Table 3, the model M8, which employs x_3 and x_{10} , gives the best two-variable linear inference for purity. Let z denote the purity with the unit of mol%. M8 is expressed by

$$\text{M8: } z = -2.3016x_3 + 0.9610x_{10} + 118.27 \quad (9)$$

This suggests that an increase of 1°C in x_3 will lead to a decrease of approximate 2.3mol% in purity, while an increase of 1°C in x_{10} will result in an increase of about 1mol% in purity.

As in conversion inference, introducing second-order terms into the inferential model can significantly improve the inference performance for purity. The best two-variable second-order inferential model is also a combination of x_3 and x_{10} . It is given by:

$$\text{M9: } z = -0.047615 x_3^2 - 48.0817 x_3 + 0.267950 x_3 x_{10} - 17.0059 x_{10} - 0.007138 x_{10}^2 + 3133.85 \quad (10)$$

The corresponding correlation coefficients for fitting and testing respectively reach 0.9992 and 0.9977, compared to 0.9947 and 0.9847 for linear inference. The standard deviations are reduced from 1.6004 to 0.6363 and from 2.1905 to 0.9357 for fitting and testing, respectively.

When a third-order model is employed, the inference performance can be further improved. As shown in Table 3, the third-order model M10, which employs x_5 and x_{10} , outperforms the second-order model M9. M10 is described by

$$\begin{aligned} \text{M10: } z = & -0.00388225 x_5^3 + 1.090412 x_5^2 - 116.2423 x_5 - 0.00074674 x_5^2 x_{10} + 0.369668 x_5 x_{10} \\ & - 0.00094052 x_5 x_{10}^2 - 15.3741 x_{10} + 0.016031 x_{10}^2 + 0.00013517 x_{10}^3 + 3860.38 \quad (11) \end{aligned}$$

For both model identification and model testing, the resulting correlation coefficients are sufficiently high (larger than 0.9997) and the standard deviations are sufficiently small (less than 0.3). As discussed in conversion inference, there is no need to further increase the model order for purity inference.

Three-variable models are also shown in Table 3 for purity inference. The best three-variable linear model M11 has only limited performance improvement compared with the two-variable linear model M8, while an extra measurement is introduced. The three-variable second-order model M12 and the two-variable third-order model M10 have the same number of parameters. It is seen from Table 3 that M10 is superior to M12 in both correlation coefficients and standard deviations. Thus, M10 is recommended for purity inference.

6. MODEL TESTING

In addition to the statistical analysis discussed in the previous section, numerical simulations have also been carried out to illustrate the effectiveness of the proposed inferential models for conversion and purity in ETBE reactive distillation. For the 54 observations for model identification and the 33 observations for model testing, conversion values are predicted with the recommended inferential model M5 and purity values are estimated with the recommended inferential model M10. Then, these computed values are compared with the actual sampling values. The prediction error is defined as

$$\text{Prediction error} = \text{actual value} - \text{prediction value} \quad (12)$$

Prediction errors for conversion inference are plotted in Figs. 4 and 5, where Fig. 4 is based on the 55 observations for model identification and Fig. 5 corresponds to the 33 observations for model testing.

Portraits of prediction errors for purity inference are depicted in Figs. 6 and 7, where Fig. 6 is drawn with the 55 observations for model identification and Fig. 7 is plotted with the 33 observations for model testing.

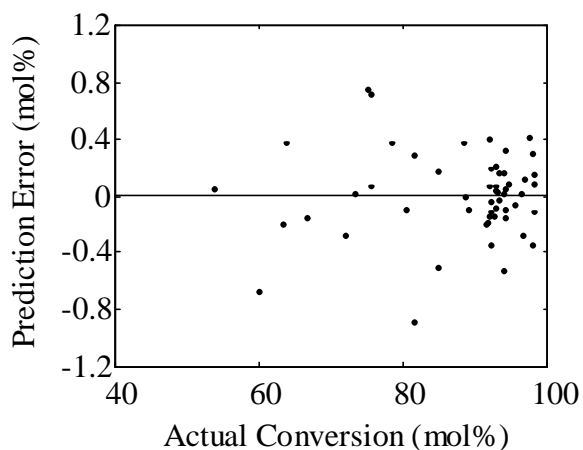


Figure 4. Errors of conversion inference with the 55 observations for model identification.

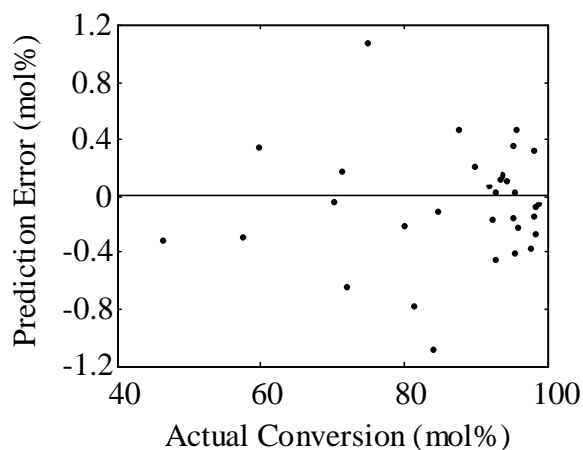


Figure 5. Errors of conversion inference with the 33 observations for model testing.

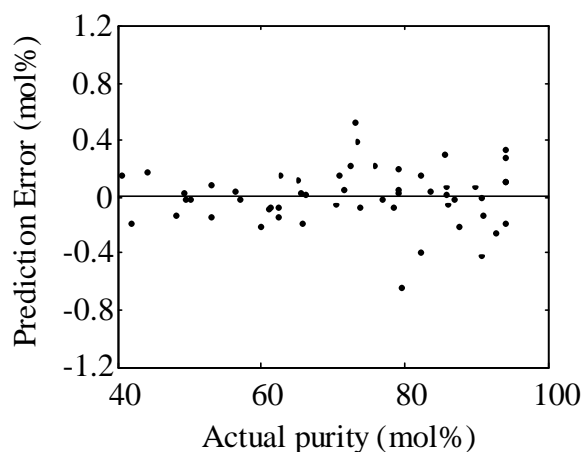


Figure 6. Errors of purity inference with the 55 observations for model identification.

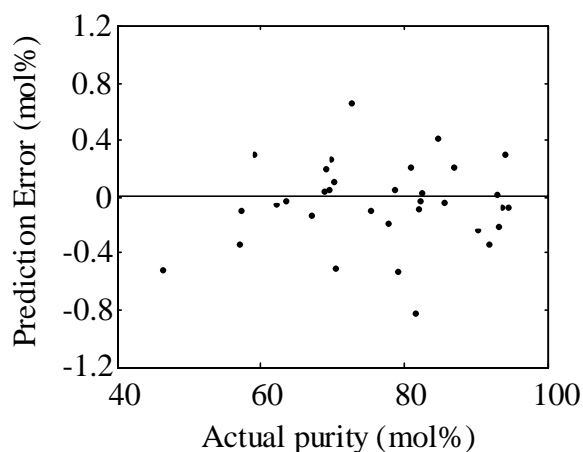


Figure 7. Errors of purity inference with the 33 observations for model testing.

It is clearly seen from Figs. 4 through 7 that the prediction errors for both conversion and purity are very small with the recommended inferential models, again suggesting the good performance of the inferential models.

7. CONCLUSIONS

In reactive distillation of ETBE, two important variables, conversion and purity, are difficult to measure economically and reliably. This work has shown that both conversion and purity can be effectively inferred from multiple process temperatures, which can be easily measured using thermocouples. The development of inferential models is a key element for inference of the conversion and purity.

A ten-stage pilot scale RD process for ETBE synthesis has been considered with six temperature measurements. Two- and three-variable inferential models with orders ranging from one to three were identified using regression method. The models were then tested with a different group of sampling data. According to the correlation coefficients and standard deviations, two-variable third-order nonlinear inferential models, M5 and M10, were

recommended for conversion and purity, respectively. Both the models were nonlinear combinations of the temperature at the bottom of the reactive section and the reboiler temperature. Higher-order or three-variable or higher-order models were shown to be unnecessary. Good performance of the recommended models was demonstrated.

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