CHEMICAL ENGINEERING TRANSACTIONS
VOL. 70, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

**ISBN** 978-88-95608-67-9; **ISSN** 2283-9216
DOI: 10.3303/CET1870231

# An Algebraic Analysis Modelling Method for Complex Reactions

Leihao Zhou, Changfang Yin, Guilian Liu*

School of Chemical Engineering and technology, Xi'an Jiaotong University, Shaanxi Provice, China, 710049
guilianliui@mail.xjtu.edu.cn.

An algebraic analysis modelling method is introduced to analyse complicated reaction system, based on the relationship between substances studied from the atomic scope. Firstly, the feasible reaction network is identified based on the transformation of the atomic matrix. Then, the model is adjusted according to the kinetic parameters, and the most suitable grey-box model is identified, and can be applied to analyse the influence of reaction parameters (including feed, temperature, pressure and residence time) on the conversion, selectivity and yield, and provide theoretical basis for adjusting and optimizing the reaction system. The proposed method has less experimental data demand, lower kinetic parameter accuracy requirement and self-correction ability, and can be easily programmed into software. An ethylene cracking reaction is studied to illustrate its application.

## 1. Introduction

In the chemical process, the reaction unit has an apparent effect to both upstream and downstream units, especially the separation unit. The study on it can provide not only the information of what happened inside reactor and the product composition, but also useful data to the reaction network optimization and energy saving. However, all of these rely on a model which can describe the reaction correctly. A good reaction model not only can be applied to study the reactions in detail, but also can predict the reaction performance before the actual operation. This brings great opportunity for factory.

In 1981, Ninshida et al. (1981) had begun to seek the way of reaction modelling, and divided different approaches into two categories, the knowledge-based methods and the logic-based methods. The former greatly relies on databases or sets of known reactions to show different possible reaction transformation rules, such as LHASA (Corey et al., 1974) and ZENETH (Parenty et al., 2013). The latter is based on the idea of Ugi and Gillespie (1971), such as RAIN and IGOR (Ugi et al., 1988), use matrices to represent the chemical structure of molecules and reaction transformation, and can consider the breaking and making of individual atom-atom bonds, which can take all possible reactions into account. Its disadvantage is that some infeasible reactions might be included in the identified reaction system.

To identify which reactions are feasible or infeasible, and choose a set of reactions to describe the whole reaction system, Arise and Mah (1987) raised the idea of independent reaction by the support of stoichiometric number theory. Based on this, the number of reactions to describe the reaction system can be identified. However, the exact reactions cannot be identified.

In order to get a more accurate model, Franceschini et al. (2008) raised a MBDOE (model-based design of experiments) method with the model optimized by repeated experiments. Thereafter, Luna et al (2014) built a MBDOE method with the process optimization and product data taken into account. This method suit for the reaction system with parameters varying in a small interval. Because of this, Galvanin et al. (2010) added the lower limit of the experimental results into this method.

Based on the predecessors, Zhang et al. (2004) raised a systematic method with model building, experiment design and process optimization combined, and molecular dynamics considered. This method is efficient in identifying independent reaction, and suits for a broader reaction condition. However, it has limited flexibility and requires a large amount of computation.

The method of Zhang et al. (2015) is extended for modelling complex reactions and predicting the performance of the reaction system under different conditions. A grey-box model is built to analyse the influence of reaction

Please cite this article as: Zhou L., Yin C., Liu G., 2018, An algebraic analysis modelling method for complex reactions , Chemical Engineering Transactions, 70, 1381-1386 DOI:10.3303/CET1870231

parameters on the conversion, selectivity and yield, and provide theoretical basis for adjusting and optimize the reaction system.

## 2. Model building methodology

### 2.1 Rearranged atom-molecular matrix

To build the model of a reaction system, it is necessary to know all the involved molecular, which is represented by a dynamic set, S. Subset R and P represent reactants and products, respectively. To make the main reaction more clearly, the elements of S are rearranged in the order from R to P. Different from the work of Zhang et al. (2015), the elements can be sorted according to the decreasing order of mole fractions in the reactor. Their relationship is represented as $R \subset S$ , $P \subset S$ and $S = R \bigcup P$ . Each element in S can be represented by the number of corresponding atoms (or function groups) included in this element. All elements can be represented together by an arranged atom-molecule matrix A. Each line corresponds an atom, while each column corresponds an element. $a_{ij}$ represents the number of the ith atom/function group contained in the j[th] element, as shown below:

$$A_{M\times N} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1N} \\ a_{21} & a_{22} & \cdots & a_{2N} \\ \vdots & \vdots & a_{ij} & \vdots \\ a_{M1} & a_{M2} & \cdots & a_{MN} \end{bmatrix} \quad a_{ij} = \begin{cases} >0 & \text{the number of the } i\text{th atom contained in the } j\text{th element} \\ =0 & \text{the } i\text{th atom is not contained in the } j\text{th element} \end{cases} \tag{1}$$

Where M is the total number of atoms involved in the reaction system, N is that of molecules.

### 2.2 Feasible reactions analysis

An n-dimensional vector, $X = (x_1, x_2, \cdots, x_j, \cdots, x_n)^T$ , is defined to indicate the stoichiometric factor of the feasible reaction. If $AX = 0$ , a feasible chemical reaction exists. However, there might be infinite solutions for *X*, and not everyone corresponds to a feasible reaction. Hence, it is necessary to identify whether a solution represents a feasible reaction or not. To solve this problem, reactions will be divided into two stages according to the difference of reactants, stage I and stage II. For stage I, the reactant of a reaction is a subset of set R, and the products should be a subset of set P. All of those subsets compose reactant set $R_1$ and product set $P_1$. For stage II, the reactants of a reaction should be a subset of set M (both set R and P) and the reactants should be a subset of the set P. All these subsets compose reactant set $R_2$ and product set $P_2$.

With all reactions assumed to be irreversible and all feed cannot appear as the product, all elements of reactant sets and products sets can be matched one by one, and their balance should be checked for stage I and stage II, respectively. If there is a balanceable reaction, a solution of *X* exists, and the stoichiometric factor of each molecular is the corresponding element of *X*. However, there are a large number of elements in the reactant set and product set, and the number of the reactant-product combinations, which is their multiply, is even more. It is difficult to identify all feasible reactions through checking the balance between reactant and product. This is the problems remaining in the method of Zhang et al. (2015). To solve this problem, an algebra method will be proposed to find feasible reactions.

In stage I, set R and P are written into a $M \times N$ arranged atom-molecule matrix A, in which R can be written as a $M \times T$ sub-matrix. If $M > T$ , choose all line of R. If $M \le T$ , choose M line randomly from R to replace the sub-matrix R, then a new atom-molecule matrix is constituted. In theory, there are $C_T^M$ new atom-molecule matrix, and can be written as $A_{0i}$ $\left(i = 0,1,2\cdots C_T^M\right)$ . Then, sub-matrix, $R_{0M}$ , can be identified through the row transform of $A_{0i}$ . If a column in sub-matrix P0 has no element less than 0, this column represents a feasible reaction *X*, whose product is the corresponding molecular of this column, and the reactants are the molecular corresponding the element greater than 0 in this row. With a randomly chosen line, P0, multiplied by $i = 1,2,3$ and added to another line, a new line is obtained. If there is no element less than 0, a feasible reaction is identified, and its products are the matters represented by both lines. Besides, according to the theory of liner algebra, no more than $N_{ind} = M - R$ (R is the matrix order of $M_0$) linearly independent reactions can be obtained.

In stage II, a line in sub-matrix $P_0$ is respectively selected from left to right and add to sub-matrix $R_0$. Then, by the same method of stage I, the reactions of stage II can be identified.

### 2.3 Reaction network modelling

All identified *X* can be written in a stoichiometric coefficient matrix, $\varphi$ :

$$\varphi = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1R} \\ x_{21} & x_{22} & \cdots & x_{2R} \\ \vdots & \vdots & x_{jk} & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{nR} \end{bmatrix} = [X_1, X_2, \cdots, X_R] \qquad X_{jk} = \begin{cases} >0 & \text{product} \\ <0 & \text{reactant} \\ =0 & \text{not included} \end{cases} \tag{2}$$

Where, $x_{jk}$ is the stoichiometric coefficient of molecule j in the reaction k.

Then, the column vector of matrix will be divided into two parts, u vectors in stage I and v vectors in stage II. Meanwhile, the row vector will be divided into two parts, set R and set P. And, matrix $\varphi$ will be divided into four parts: $\varphi_{IR}$ , $\varphi_{IIR}$ , $\varphi_{IP}$ and $\varphi_{IIP}$ .

$$\varphi = \begin{array}{c} \\ m_1 \\ m_2 \\ \text{M} \\ m_T \\ \text{L} \\ m_{T+1} \\ m_{T+2} \\ \text{M} \\ m_N \end{array} \begin{array}{c} \begin{array}{cccccccccc} X_1 & X_2 & \text{L} & X_u & \text{M} & X_{u+1} & X_{u+2} & \text{L} & X_{u+v} \end{array} \\ \begin{bmatrix} & & & & \text{M} & & & & \\ & & & & \text{M} & & & & \\ & & \varphi_{IR} & & \text{M} & & \varphi_{IIR} & & \\ & & & & \text{M} & & & & \\ \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\ & & & & \text{M} & & & & \\ & & \varphi_{IP} & & \text{M} & & \varphi_{IIP} & & \\ & & & & \text{M} & & & & \\ & & & & \text{M} & & & & \end{bmatrix} \end{array} \qquad \Phi = \begin{array}{c} \\ m_1 \\ m_2 \\ \text{M} \\ m_T \\ \text{L} \\ m_{T+1} \\ m_{T+2} \\ \text{M} \\ m_N \end{array} \begin{array}{c} \begin{array}{cccccccccc} X_1 & X_2 & \text{L} & X_u & \text{M} & X_{u+1} & X_{u+2} & \text{L} & X_{u+v} \end{array} \\ \begin{bmatrix} & & & & \text{M} & & & & \\ & & & & \text{M} & & & & \\ & & \Phi_{IR} & & \text{M} & & \Phi_{IIR} & & \\ & & & & \text{M} & & & & \\ \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\ & & & & \text{M} & & & & \\ & & \Phi_{IP} & & \text{M} & & \Phi_{IIP} & & \\ & & & & \text{M} & & & & \\ & & & & \text{M} & & & & \end{bmatrix} \end{array} \tag{3}$$

If an element of matrix $\varphi$ is greater than 0, rewrite it as 1; if it is less than 0, rewrite it as -1. In this way, the matrix $\varphi$ will be transferred into the incidence matrix $\Phi$. Then, an $u+v$ dimension row vector *I* constituted by 0 and 1 is obtained. With $\Phi$ multiplied *I* and the rank of 0 deleted, a new matrix, $\Phi^i$ , is obtained. If $\Phi^i$ satisfies the conditions below, *I* can be a feasible reaction network vector and $\Phi^i$ can be a feasible reaction matrix.

- In the area ($\Phi_{IR}$,$\Phi_{IP}$), there must be at least one reaction. In other words, the feed must react.
- In the area ($\Phi_{IR}$,$\Phi_{IIR}$), the sum of each row must be less than 0 after elementary transformation.
- In the area ($\Phi_{IP}$,$\Phi_{IIP}$), the sum of each row must be greater than 0 after elementary transformation.
- In the area of products ($\Phi_{IP}$,$\Phi_{IIP}$), each row must have one element not equal to 0.
- In matrix $\Phi^i$ , not all elements within each row are 0 to make sure all molecular take part in the reaction.
- All elements of area $\Phi_{IR}$ should not be greater than 0.
- All elements of area $\Phi_{IIP}$ should not be less than 0.

Once a feasible reaction network vector is identified, a feasible reaction network's rival model, $\varphi^i$ , can be obtained according $\varphi \times I$ and with the rank of 0 deleted.

In this procedure, more screening is used. Hence, these rules are more succinctly than previous work.

### 2.4 Rival model option

In this part, a molecular dynamics way will be raised to calculate models and an imaginary number m will be used to estimate rival models. Furthermore, reactants will be assumed as well mixed and all molecules' residence time is long enough. To distinguish the rival model, whose result is in better agreement with the real reaction, the reaction rate constant of all feasible reactions (k) or the activation energy (Ea) should be identified. What's more, the real data of feed and products at given T and P are also important.

The reaction rate can be calculated according to Eq(4).

$$v_i = k_i C_i \ . \tag{4}$$

The concentration of each molecular can be identified according to the state equation, as shown by Eq(5).

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT} = \frac{Px_i}{RT} \tag{5}$$

Based on this, Eq(4) can be written as:

$$v_i = k_i \frac{Px_i}{RT} \tag{6}$$

Then, the reaction rate of each reaction can be substituted into the rival model. Firstly, all elements of 1 in vector I will be represented as the corresponding reaction rate and all elements of 0 will be deleted, then the new vector will be rewritten as a column vector, v. With $\varphi^i$ multiplied $v$ , column vector r is obtained, and its element represents the change rate of corresponding molecular (negative means consumption and positive means

generation). Meanwhile, mi is used to represent the total molar variation calculated according to molecular i, and can be calculated according to Eq(7) based on the change rate of every molecular, $g_i$

$$m_i = \frac{r_i}{g_i} \tag{7}$$

In ideal situation, $m_i$ should be a constant no matter which molecular is used to calculate. However, it may be different from each other because of the accuracy of the model. The dispersion degree of $m_i$ shows the error between rival model and real reaction system. A weighted variance, W, can be used to evaluate the model, and can be calculated by Eq(8). The better a model is, the smaller the value of W will be.

$$W = \sqrt{(\overline{m} - m_1)^2 x_1 + (\overline{m} - m_2)^2 x_2 + \cdots + (\overline{m} - m_n)^2 x_n} \tag{8}$$

Where $\overline{m}$ is the weighted average of $m_i$ .

## 3. Illustrative example: thermal cracking of ethane

Based on Wu's (2011) paper, the temperature and pressure of a thermal cracking reaction of ethane are 1,102.45 K and 1.55 bar respectively. The mole fractions of main molecular in feed and products are displayed in Table 1. What's more, the increasing rate of feed volume is 1.54.

*Table 1: Feed and product data*

| | $C_2H_6$ (a) | $H_2$(b) | $C_2H_4$(c) | $CH_4$(d) | $C_3H_6$(e) | $C_3H_8$(f) | $C_2H_2$(g) | Others |
|---|---|---|---|---|---|---|---|---|
| Feed | 99.3 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0 |
| Product | 26.7 | 35.2 | 33.1 | 3.6 | 0.3 | 0.3 | 0.2 | 0.6 |

### 3.1 Atom-molecular matrix analysis

According to de reaction mechanism, the basic atom or function group participating in the reactions are C and H, and the reactant set only include $C_2H_6$. Then the molecular can be rearranged by their mole fraction, and the rearranged atom-molecular matrix $A_0$ is obtained.

$$A_0 = \begin{array}{c} \\ C \\ H \end{array} \begin{array}{c} \begin{array}{ccccccc} a & b & c & d & e & f & g \end{array} \\ \begin{bmatrix} 2 & 0 & 2 & 1 & 3 & 3 & 2 \\ 6 & 2 & 4 & 4 & 6 & 8 & 2 \end{bmatrix} \end{array} \tag{9}$$

### 3.2 Generating feasible reactions

In this system, the number of molecular taken into consideration is 7, while the rank of $A_0$ is 2. Hence, the number of independent reactions should be no more than 5. In stage I, the reaction set only includes a, and only the first line should be simplified. Thereafter, $A_0$ is transferred into $A_1$. According to this matrix, 5 independent reactions are identified in stage I and displayed in Figure 1a.

$$A_1 = \begin{array}{c} \\ C \\ H \end{array} \begin{array}{c} \begin{array}{ccccccc} a & b & c & d & e & f & g \end{array} \\ \begin{bmatrix} 1 & 0 & 1 & 0.5 & 1.5 & 1.5 & 1 \\ 0 & 2 & -2 & 1 & -3 & -1 & -4 \end{bmatrix} \end{array} \tag{10}$$

In stage II, the reactions can be identified in the similar procedure and are shown in Figure 1b. Among these 10 reactions, $X_E$ is infeasible in chemical thermodynamics, and is deleted.

$$\begin{array}{l} X_1 \\ X_2 \\ X_3 \\ X_E \\ X_4 \end{array} \left\{ \begin{array}{rcrcl} a & = & c & + & b \\ 2a & = & c & + & 2d \\ 2a & = & d & + & f \\ 3a & = & 3d & + & e \\ a & = & g & + & 2b \end{array} \right\}$$

a

$$\begin{array}{l} X_5 \\ X_6 \\ X_7 \\ X_8 \\ X_9 \end{array} \left\{ \begin{array}{rcrcl} f & = & b & + & e \\ c & = & g & + & b \\ f & = & c & + & d \\ c + a & = & d & + & e \\ e & = & d & + & g \end{array} \right\}$$

b

*Figure 1: independent reactions for stage I and II*

### 3.3 Feasible reaction network modelling

According to the 9 identified feasible reactions, the stoichiometric coefficient matrix, $\varphi$ can be obtained and transferred into the incidence matrix $\Phi$, as displayed in Figure 2. Thereafter, 3 rival models will be used to compare a lot of models. The feasible reaction network vector *I* is displayed in Table 2. For model 1, 2 and 3, the corresponding matrix, $\Phi^1$, $\Phi^2$ and $\Phi^3$ are displayed in Figure 3.

$$\varphi = \begin{array}{c} \\ a \\ \dots \\ b \\ c \\ d \\ e \\ f \\ g \end{array} \begin{array}{c} \begin{array}{ccccccccc} X_1 & X_2 & X_3 & X_4 & \vdots & X_5 & X_6 & X_7 & X_8 & X_9 \end{array} \\ \begin{bmatrix} -1 & -2 & -2 & -1 & \vdots & 0 & 0 & 0 & -1 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 1 & 0 & 0 & 2 & \vdots & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & \vdots & 0 & -1 & 1 & -1 & 0 \\ 0 & 2 & 1 & 0 & \vdots & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & \vdots & 1 & 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 0 & \vdots & -1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & \vdots & 0 & 1 & 0 & 0 & 1 \end{bmatrix} \end{array} \qquad \Phi = \begin{array}{c} \\ a \\ \dots \\ b \\ c \\ d \\ e \\ f \\ g \end{array} \begin{array}{c} \begin{array}{ccccccccc} X_1 & X_2 & X_3 & X_4 & \vdots & X_5 & X_6 & X_7 & X_8 & X_9 \end{array} \\ \begin{bmatrix} -1 & -1 & -1 & -1 & \vdots & 0 & 0 & 0 & -1 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 1 & 0 & 0 & 1 & \vdots & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & \vdots & 0 & -1 & 1 & -1 & 0 \\ 0 & 1 & 1 & 0 & \vdots & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & \vdots & 1 & 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 0 & \vdots & -1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & \vdots & 0 & 1 & 0 & 0 & 1 \end{bmatrix} \end{array}$$

*Figure 2: Matrix $\varphi$ and incidence matrix $\Phi$*

*Table 2: A part of reaction network vector*

| Model | ***I*** |
|---|---|
| 1 | 1, 1, 0, 0, 1, 0, 0, 1, 1 |
| 2 | 1, 0, 1, 0, 0, 0, 0, 1, 1 |
| 3 | 1, 0, 1, 0, 1, 0, 1, 0, 1 |

$$\Phi^1 = \begin{array}{c} \\ a \\ \dots \\ b \\ c \\ d \\ e \\ f \\ g \end{array} \begin{array}{c} \begin{array}{cc} X_1 & X_2 \end{array} \\ \begin{bmatrix} -1 & -1 \\ \dots & \dots \\ 1 & 0 \\ 1 & 1 \\ 0 & 1 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix} \end{array} \quad \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{c} \vdots \\ X_5 \end{array} \\ \begin{bmatrix} \vdots & 0 \\ \dots & \dots \\ \vdots & 1 \\ \vdots & 0 \\ \vdots & 0 \\ \vdots & 1 \\ \vdots & -1 \\ \vdots & 0 \end{bmatrix} \end{array} \quad \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{cc} X_8 & X_9 \end{array} \\ \begin{bmatrix} -1 & 0 \\ \dots & \dots \\ 0 & 0 \\ -1 & 0 \\ 1 & 1 \\ 1 & -1 \\ 0 & 0 \\ 0 & 1 \end{bmatrix} \end{array}$$

a

$$\Phi^2 = \begin{array}{c} \\ a \\ \dots \\ b \\ c \\ d \\ e \\ f \\ g \end{array} \begin{array}{c} \begin{array}{cc} X_1 & X_3 \end{array} \\ \begin{bmatrix} -1 & -1 \\ \dots & \dots \\ 1 & 0 \\ 1 & 0 \\ 0 & 1 \\ 0 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix} \end{array} \quad \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{c} \vdots \\ \dots \end{array} \\ \begin{bmatrix} \vdots \\ \dots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \end{bmatrix} \end{array} \quad \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{cc} X_8 & X_9 \end{array} \\ \begin{bmatrix} -1 & 0 \\ \dots & \dots \\ 0 & 0 \\ -1 & 0 \\ 1 & 1 \\ 1 & -1 \\ 0 & 0 \\ 0 & 1 \end{bmatrix} \end{array}$$

b

$$\Phi^3 = \begin{array}{c} \\ a \\ \dots \\ b \\ c \\ d \\ e \\ f \\ g \end{array} \begin{array}{c} \begin{array}{ccc} X_1 & X_3 & \vdots \end{array} \\ \begin{bmatrix} -1 & -1 & \vdots \\ \dots & \dots & \dots \\ 1 & 0 & \vdots \\ 1 & 0 & \vdots \\ 0 & 1 & \vdots \\ 0 & 0 & \vdots \\ 0 & 1 & \vdots \\ 0 & 0 & \vdots \end{bmatrix} \end{array} \quad \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{ccc} X_5 & X_7 & X_9 \end{array} \\ \begin{bmatrix} 0 & 0 & 0 \\ \dots & \dots & \dots \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 1 & 1 \\ 1 & 0 & -1 \\ -1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{array}$$

c

*Figure 3: corresponding matrix*

For model 1, it's easy to find out that it is infeasible as the sum of row f cannot be greater than 0. Model 2 is feasible although the area of $\Phi_{IIP}$ has elements less than 0, as $\Phi^2$ will satisfy all conditions with $X_1$, $X_8$ and $X_9$ added. Similarly, model 3 is feasible as $\Phi^3$ can be made to satisfy all conditions through rank transformation.

### 3.4 Rival model compare

In this part, reaction system data taken from Basic organic chemical technology (Wu, 2011) will be used to estimate rival models. Based on the data of Sundaram and Froment (1976), the reaction rate constants under 1,102.45 K are inferred and displayed in Table 3. Reaction 4 and 6 are taken out of consideration as their reaction rate constants are too small. According to Eq(6), the reaction rate can be calculated, and are displayed in Table 3 as well.

*Table 3: Inferred reaction rate constant and reaction rates*

| Reaction number | Reaction rate constant ($s^{-1}$ or $m^3 \cdot mol^{-1} \cdot s^{-1}$) | Reaction rate ($mol \cdot m^{-3} \cdot s^{-1}$) | Reaction number | Reaction rate constant ($s^{-1}$ or $m^3 \cdot mol^{-1} \cdot s^{-1}$) | Reaction rate ($mol \cdot m^{-3} \cdot s^{-1}$) |
|---|---|---|---|---|---|
| 1 | 24.9226 | 5.5198 | 7 | 0.0221 | 4.3657 |
| 2 | 0.9683 | 0.0475 | 8 | 0.1875 | 0.0074 |
| 3 | 0.9112 | 0.0447 | 9 | 0.0324 | 0.6386 |
| 5 | 0.0203 | 3.9982 | | | |

For model 2 and 3, the corresponding matrix $\varphi^2$ and $\varphi^3$ are displayed in Figure 4a and 4b, respectively, and $r^i$ are displayed in Table 4. The real change rates calculated according to Table 1 are listed in Table 4 as well.

*Table 4: Change rates of molecular ($mol \cdot m^{-3} \cdot s^{-1}$)*

| Molecular | Model 2 | Model 3 | $g_i$ | $m_i$ (2) | $m_i$ (3) | Molecular | Model 2 | Model 3 | $g_i$ | $m_i$ (2) | $m_i$ (3) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6$ | -26.93 | -26.75 | 0.378 | 71.25 | 70.75 | $CH_4$ | 1.13 | 0.97 | 0.0347 | 32.60 | 27.83 |
| $H_2$ | 24.92 | 24.94 | 0.352 | 70.80 | 70.76 | $C_3$ | 1.07 | 0.86 | 0.006 | 177.71 | 142.77 |
| $C_2H_4$ | 24.74 | 24.94 | 0.328 | 75.41 | 76.05 | $C_2H_2$ | 0.032 | 0.032 | 0.002 | 16.21 | 16.21 |

According to Table 4, the m for different molecular in every model can be identified. Furthermore, the weighted variance W of model 2 and 3 calculated according to Eq(8), are W2 = 2.02 and W3 = 2.27, respectively. Since W2 is less than W3, model 2 is better to describe the reaction under the condition of 155 kPa and 1,102.45K.

## 4. Conclusions

A new approach for reaction model building is proposed in this paper. Based on this method, all possible reactions and frameworks and a plenty of rival model can be identified to describe the reaction system based on only a set of reaction data. The variance can be used to judge every model, and the lower variance corresponds better model. The model can be used to predict the reaction system in a certain amount of reaction conditions and optimize the chemical production. However, if the reaction condition changes significantly, the reactions involved in the reaction system can be different, and the identified reaction model does not suit anymore. How to enlarge the scope of application or change the model along operating parameter will be considered in further.

**Acknowledgement**

Financial support provided by the National key research and development program of China (2017YFB0602603) are gratefully acknowledged.

**References**

Corey E.J., Howe W.J., Pensak D.A., 1975, Computer-assisted synthetic analysis, methods for machine generation of synthetic intermediates involving multi-step look-ahead, Cheminform, 6(8), 7724–7737.

Franceschini G., Macchietto S., 2008, Novel anticorrelation criteria for design of experiments: Algorithm and application, AIChE Journal, 54(12), 3221-3238.

Galvanin F., Barolom M., Bezzo F., Macchietto S., 2010, A back off strategy for model-based experiment design under parametric uncertainty, AIChE Journal, 56(8), 2088-2102.

Luna M., Martinez E.A., 2014, A bayesian approach to run-to-run optimization of animal cell bioreactors using probabilistic tendency models. Industrial & Engineering Chemistry Research. 53(44), 17252-17266.

Ninshida N., Stephanopoulos G., Westerberg A.W., 1981, A review of process synthesis, AIChE Journal, 27(3), 321-351.

Oláh K., 1987, Independence of chemical reactions, Reaction Kinetics & Catalysis Letters, 33(1), 9-15.

Parenty A.D., Button W.G., Ott M.A., 2013, An expert system to predict the forced degradation of organic molecules, Molecular Pharmaceutics, 10(8), 2962-2974.

Sundaram K.M., Froment G.F., 1997, Modeling of thermal cracking kinetics-I: thermal cracking of ethane, propane and their mixtures, Chemical Engineering Science, 32(6), 601-608.

Ugi I.K., Bauer J., Baumgartner R., Fontain E., Forstmeyer D., 1988, Computer-assistance in the design of syntheses and a new generation of computer-programs for the solution of chemical problems by molecular logic. Pure and Applied Chemistry, 60(11), 1573-1586.

Ugi I.K, Gillespie P., 1971, Representation of chemical systems and interconversion by BE matrices and their transformation properties, Angewandte Chemie International Edition in English, 10(12), 914-915.

Wu Z., 2011, Basic organic chemical technology, Chemical Industry Press, Beijing, China.

Zhang W., 2004, Model building methodology for complex reaction systems, PhD Thesis, University of Manchester Institute of Science and Technology, Manchester, UK.

Zhang W., Binns M., Theodoropoulos C., Kim J.K., Smith R., 2015, Model building methodology for complex reaction systems, Industrial & Engineering Chemistry Research, 54(16), 4603-4615.