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ITJ

ISSN 1812-5638

INFORMATION TECHNOLOGY JOURNAL

ANSI*net*

Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

On-line Production Quality Prediction for a Commercial Naphtha Catalytic Reforming Process

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Abstract: In this study, a 20-lumped kinetics model and a linear Partial Least Squares (PLS) model are applied to the on-line aromatics yield prediction for a commercial Continuous Catalyst Regeneration (CCR) platforming process. The off-line simulation results of the two models are both excellent and then a valid on-line prediction and revision strategy is adopted in the CCR process. The average deviation between on-line predicted and actual aromatics yield is 0.54% (by mass) and 0.62% respectively which is nearly equal to the off-line prediction performance. The difference between the two models is also studied. A software package, named APC-Sensor, including the two models and the on-line prediction and revision strategy, has been successfully applied in the CCR process.

Key words: Kinetic model, linear partial least squares model, on-line prediction, catalytic reforming, aromatics yield

INTRODUCTION

Catalytic naphtha reforming is a very important process for producing high octane gasoline and aromatics feedstock in petrochemical industry (Li, 2010). Hydrogen and lighter hydrocarbons are also obtained as byproducts. The catalytic reforming processes in the world differ in the catalyst type, the catalyst regeneration procedure (cyclic, semiregenerative, or continuous), or the structure of the process flowsheet.

A normal commercial catalytic reforming process is made up of 3 or 4 adiabatic reactors in series with intermediate heaters, as shown in Fig. 1. The naphtha which consists of more than three hundred components, is mixed with recycled hydrogen and heated to the desired temperature before entering the first radial flow reactor. Each of the components undergoes various reactions.

While it is impossible to identify all the constituent components in the naphtha and account for all the reactions in the reformers, attempts have been made to model naphtha by considering groups of components (i.e., kinetics lumps) taking part in reforming reactions. Accordingly, various lumped kinetics models to represent catalytic reforming reactions have been reported in the literature which have different levels of sophistication (Smith, 1959; Kmak and Stuckey, 1973; Ramage *et al.*, 1980; Froment, 1987; Weng *et al.*, 1994; Weng *et al.*, 1994; Xie *et al.*, 1995; Taskar and Riggs, 1997; Joshi *et al.*, 1999; Ancheyta-Juarez and Villafuerte-Macias, 2000; Ancheyta-Juarez *et al.*, 2001; Rahimpour *et al.*, 2003;

Zhou *et al.*, 2004; Hou *et al.*, 2007; Rodriguez and Ancheyta, 2011; Xie *et al.*, 1996; Liu *et al.*, 2004).

The accuracy of the corresponding lumped kinetics models depends on many kinds of factors. One of the most important aspects is the level of detail of the lumped kinetics model used for predicting reformat composition.

However, detailed kinetics models are not always useful for industrial application. For many domestic reforming plants, farther subdivision of the lumps is not allowed as the limited laboratory conditions. In addition, detailed kinetics model results in estimating of too many kinetics parameters and calculating colossal differential equations. When the models are used to the on-line application, it is impossible for the detailed ones to further satisfy the requirement of real time, convenience, stability and reliability. Thus a simple first-principle model of catalytic reforming with 20 lumps was proposed in a previous work (Xie *et al.*, 1996). The agreement between predicted and commercially observed results is very good.

As a CCR process aiming to yield aromatics, the real time display of aromatics yield is very important for the stable operation and advanced process control. Compared with on-line analyzers, the on-line prediction technology using models is proved to be more economical and real-time (Xie *et al.*, 1995). In section 2 and 3, the 20-lumped process model which is simplified firstly and a simpler linear model including 12 process variables are presented respectively. Their off-line prediction performances of the aromatics yield for a CCR process are both described. In section 4, the two obtained models are

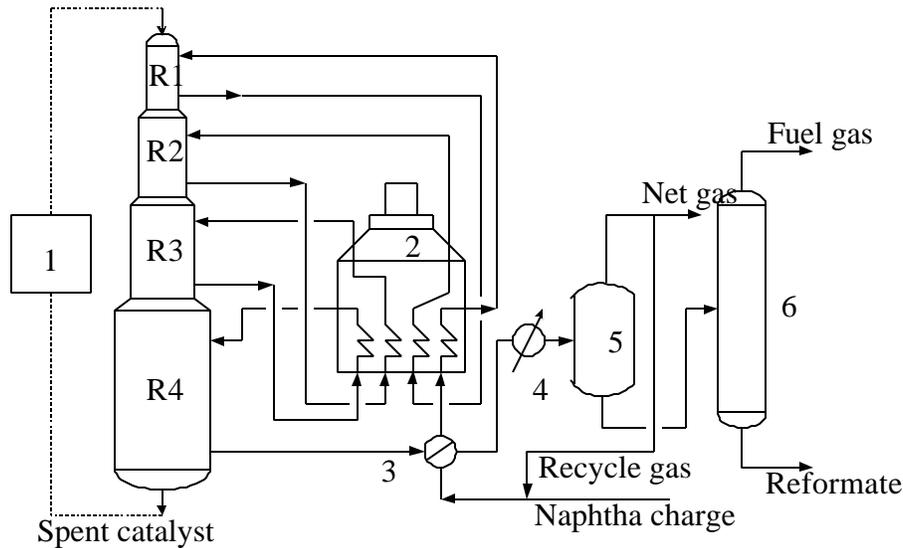


Fig. 1: A process flow diagram of CCR platforming, 1: Regeneration section, 2: Furnace, 3: Exchanger, 4: Cooler, 5: Flash separator, 6: Stabilizer, R1~R4-reformer

applied to the on-line aromatics yield prediction for the CCR process. An on-line prediction and revision strategy is described subsequently. The difference between the two models is also studied.

KINETICS MODEL AND PER- FORMANCE

In the 20-lumped kinetics model (Hou *et al.*, 2006), the reforming reaction network undergone by all the 20 lumps is shown in Fig. 2. All the 31 rate equations are nonlinear pseudo-monomolecular in nature, with the rate coefficients obeying the Arrhenius law.

For the radial flow reactors, the global material and enthalpy balance equations can be described as follows:

$$d\bar{Y}/dR = 2\pi R \cdot H / (LHSV \cdot V_c) \cdot K_r \cdot \bar{Y} \quad (1)$$

$$dT/dR = 2\pi R \cdot H / (LHSV \cdot V_c) \cdot \sum_{j=1}^{17} (r_j \cdot \Delta H_j) / (\bar{C}_p \cdot \bar{Y}) \quad (2)$$

where, \bar{Y} is the vector of molar flow rates including 20 lumps and H_2 ; R is the radius of catalyst bed.

Equation 1 and 2 are solved by a mixed numerical algorithm of fourth order Runge-Kutta and Gear.

To decrease the difficulty of parameter estimation, we take activation energies (E_c), pressure exponents (θ) from the literature (Froment, 1987) and only estimate the 31 frequency factors (k_0) considering the estimation difference of parameters E_c , θ and un-modeling kinetics.

The procedure of parameter estimation is solved by an unstrained optimization problem and the objective function is:

$$\min J(k_0) = \frac{1}{S} \sum_{k=1}^S \left(\sum_{j=1}^m (y_{k,j}^{cd} - y_{k,j})^2 + \sum_{i=1}^4 (T_{k,i}^{cd} - T_{k,i})^2 \right) \quad (3)$$

where, S m are the number of samples and focused components respectively. The operating and assay data of the commercial CCR process, in which the input and output flowmeter values are firstly revised by material balance, are applied to estimating k_0 .

Originally, the reactor model is integrated with models of other key units (such as the flash separator) of the CCR process. As there exists a recycle between the reactors and the flash separator as shown in Fig. 1, an iterative solution is required which significantly increases the computation time. In this study, the composition of recycle hydrogen is considered as known and replaced by latest analysis value. The iterative algorithm is then ignored and only the reactors are considered. After the model is simplified, the time for solving the model equations reduces from 15~60 sec to only about 0.1 sec which is very important considering the on-line prediction runs every about 10 sec. On the other hand, there isn't matrix inverse calculation in the solution of both the process model and corresponding parameter estimation which is also very important in view of the higher reliability requirement of on-line application.

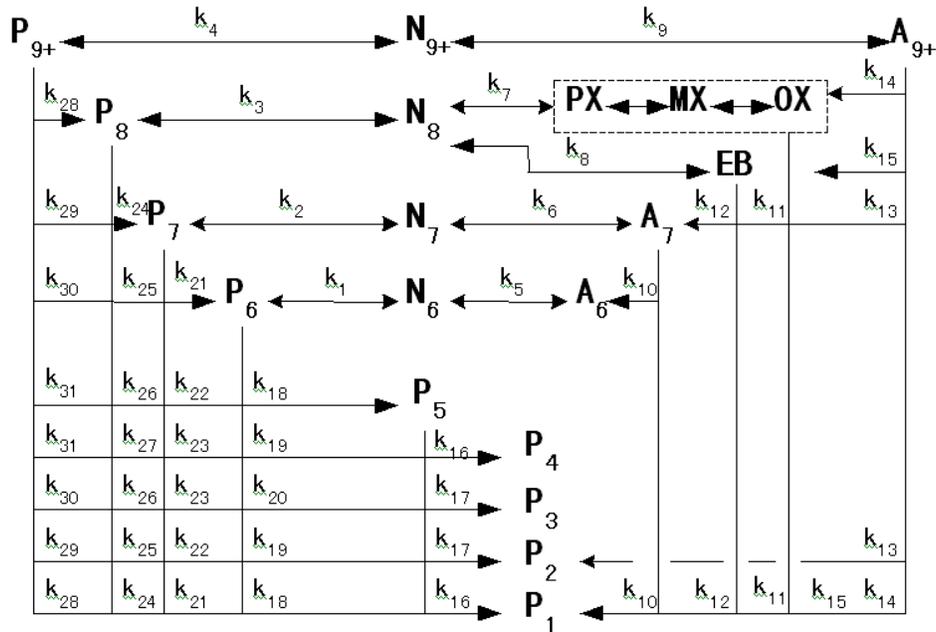


Fig. 2: Reaction scheme for naphtha reforming

Table 1: Predicted aromatics yields and deviations by the 20-lumped kinetics model and the linear PLS model

Testing samples	Actu.	Pred. by model 1*	Dev. by model 1	Pred. by model 2*	Dev. by model 2
1	69.11	68.12	-0.99	69.33	0.22
2	69.44	70.31	0.87	70.61	1.17
3	70.28	70.41	0.13	69.45	-0.83
4	70.38	70.11	-0.27	69.83	-0.55
5	68.87	67.91	-0.96	68.41	-0.46
6	69.97	69.58	-0.39	68.59	-1.38
7	69.96	70.31	0.35	70.02	0.06
8	68.99	69.53	0.54	68.55	-0.44
9	67.38	67.47	0.09	68.23	0.85
10	68.36	68.01	-0.35	68.21	-0.15
11	68.41	68.72	0.31	68.76	0.35
12	68.10	68.35	0.25	68.22	0.12
13	67.46	67.91	0.45	68.25	0.79
14	66.89	67.14	0.25	68.36	1.47
15	68.36	67.92	-0.44	67.32	-1.04
16	68.12	67.43	-0.69	67.88	-0.24
17	67.23	67.02	-0.21	67.76	0.53
18	67.20	67.51	0.31	66.77	-0.43
19	67.68	67.35	-0.33	67.03	-0.65
20	67.79	67.21	-0.58	67.10	-0.69
21	67.15	67.99	0.84	67.81	0.66
22	66.89	67.31	0.42	67.03	0.14
23	66.86	67.28	0.42	67.42	0.56
24	67.99	68.45	0.46	67.59	-0.40
25	67.86	67.99	0.13	67.53	-0.33

*Model 1 represents the 20-lumped model; model 2 represents the linear PLS model

About 33 groups of commercial data for several months, in which the feedstock charge varies from 91 to 97% and the latent feedstock aromatics content varies from 53 to 62%, are used to test the model performance of our 20-lumped kinetics model. Only 8

samples are selected for estimating the 31 parameters. The prediction results of the other 25 samples are listed in Table 1. The average absolute deviation between predicted and actual aromatics yield is only 0.44% (by mass). All the deviations vary from -0.99 to 0.87%. Because the reaction network has changed nothing, the prediction accuracy of the simplified model is still equivalent to that of the previous model (Xie *et al.*, 1996).

Obviously, the simplified 20-lumped model is appropriate to the on-line prediction of aromatics yield for the CCR process as its high stability, rapid computation speed and excellent simulation accuracy.

LINEAR PLS MODEL AND PERFORMANCE

Most of process variables, such as feedstock charge, feedstock components, reformer inlet temperature, molar hydrogen-to-oil ratio and reaction pressure, are considered by using the above 20-lumped model. The laws of their influence on the aromatics yield are dissimilar. Combining the analysis in theory, we propose a simpler linear model including about 12 variables which cover all process variables influencing the aromatics yield greatly.

Because all the commercial data sets are clustered within a very narrow operating area, ill-conditioned regression matrix may be unavoidable. The linear correlation among 12 input variables is also possible.

Partial Least Squares (PLS) regression method is proved to be a widely used multivariate regression technique to solve these problems (Yin, 1998; Kourti, 2002).

PLS method is used to extract the information contained in available process data and to project it into a low-dimensional space defined by new variables called latent variables. It means that the dimensions of two sets of data (an $m \times n_x$ input data set X and an $m \times n_y$ output data set Y) are decomposed simultaneously into two lower dimensional score matrices T ($m \times k$) and U ($m \times k$) which represent the projection of the original matrices X and Y onto the latent variable space, plus two residual matrices E ($m \times n_x$) and F ($m \times n_y$) which contain the part of X and Y that is left out of the regression:

$$X = TP^T + E \quad (4)$$

$$Y = UQ^T + F \quad (5)$$

The latent variables are aligned along the k columns of the two score matrices, T and U and are ordered in such a way that the amount of information (variance) of the original data described by each variable decreases as the number of latent variables increasing. The PLS transformation is performed so that the score vectors of each *i*th latent variable are mutually related through an inner linear relationship:

$$u_i = b_i t_i + h_i \quad (6)$$

where b_i is a coefficient determined by minimizing the norm of the residual vector h_i . An iterative solution based on the PLS algorithm is used to make t_i and u_i keeping more information of the other one, respectively. No matrix inverse is adopted in the iterative algorithm.

About 47 groups of commercial data which are contemporaneous with the samples in section 2, are used to test the performance of the linear PLS regression model. Here 22 groups of data are selected as training samples and the same 25 samples, as shown in section 2, are regarded as testing samples. The optimal number of latent variables *k* is assessed by cross-validation method which is the most reliable and widely used method. Two latent variables are testified to be optimal for the aromatics yield prediction.

The prediction results of the 25 testing samples are also listed in Table 1. The agreement between predicted aromatics yield by the linear PLS model and commercially observed value is very good too. The average absolute deviation between predicted and actual aromatics yield is only 0.58%. All the deviations vary from -1.38 to 1.47%. From Table 1, it is also observed that the prediction

performances of the two models are almost comparative for commercial applications.

ON-LINE PREDICTION OF AROMATICS YIELD

As mentioned in section 2 and 3, both the 20-lumped kinetics model and the linear PLS model are proved to be simple, accurate and reliable for the prediction of aromatics yield. However, more techniques should be adopted when applying the two models to the commercial on-line prediction. Firstly, on-line revision of the model parameters is essential because of the frequent change of the feedstock component and charge, the operating conditions or the outer environment.

In the CCR process, as input variables of the two models, the volume flow of feedstock and recycle hydrogen, the four inlet temperatures and pressures, can be obtained from the database of real-time DCS (distributed control system); while the component and density of feedstock and recycle hydrogen only can be got from laboratory 3 or 4 times every week. The component and density of reformate which are necessary for calculating actual aromatics yield, are assayed one time every day. Consequently, an on-line prediction and revision strategy is described as follows: (1) the component and density of feedstock and recycle hydrogen are replaced by the latest assay values and assumed to be constant till new data present, in view of little change of the character of feedstock within two or three days; (2) the latest sequential 12 samples are selected to estimate the model parameters for the first time; (3) because a new group of sample containing input and output assay values is obtained once every two or three days, the on-line model parameter revision is executed once every two or three days too; (4) the new sample is used for the on-line revision and simultaneously the oldest one is excluded.

Although the on-line prediction runs several thousand times every day, the prediction precision can be checked only once due to the assay frequency of aromatics components. In this study, about 76 samples of more than two months are applied to check the on-line prediction performance of the two models. The compare of on-line aromatics yield prediction precision by the two models is given in Fig. 3. It is mentionable that the samples in Fig. 3 are arrayed in sequence of time. The strategy of on-line model parameter revision mentioned above is adopted here.

From Fig. 3, it is observed that the curvilinear trends predicted by the two models are almost accordant with the trend of actual aromatics yields. It is also reportable that the prediction trend and precision of the two models are

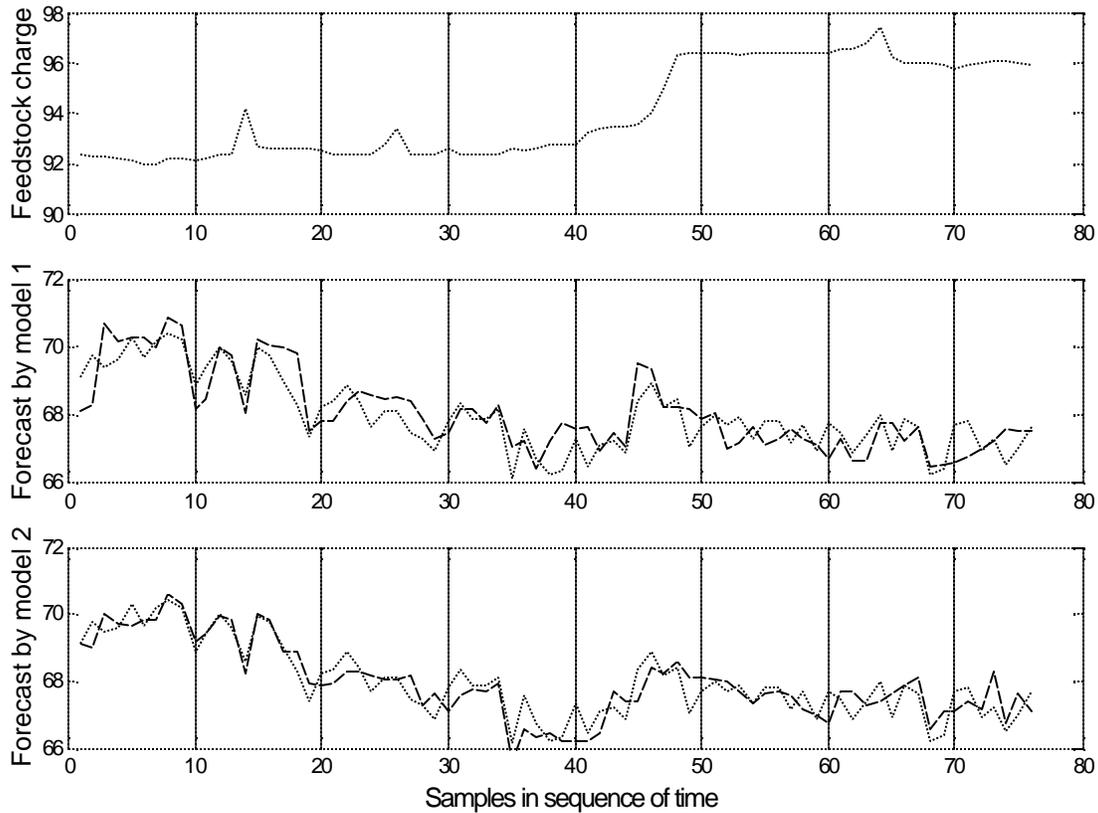


Fig. 3: Compare of on-line aromatics yield prediction precision of the CCR process by model 1 and 2 (means the actual aromatics yield, means the predicted aromatics yield; model 1 means the 20-lumped model, model 2 means the linear PLS model)

Table 2: Prediction deviations of the two models under different training sample numbers

		No. of training samples					
		4	6	8	12	16	20
The kinetics model	Average errors	0.5543	0.5501	0.5395	0.5403	0.5301	0.5237
	SSE	34.21	33.1000	32.8600	33.1800	32.3100	31.8700
The linear PLS model	Average errors	0.9458	0.8723	0.7712	0.6254	0.6458	0.6331
	SSE	125.34	89.2100	74.2100	51.2800	58.2100	56.3500

still very good when the feedstock presents a sudden and marked change (samples between 44 and 47). The average deviations between predicted and actual aromatics yield are 0.54 and 0.62%, respectively which is nearly equivalent to the off-line prediction performance mentioned in section 2 and 3.

The primary difference between the kinetics model and the linear PLS model is their sensitivities to the number of training samples selected for on-line model parameter revision. The average deviations and the error sum of squares (SSE) of the two models under different training sample numbers are given in Table 2. It is obvious that the kinetics model is almost immune when the number

of training samples widely ranges from 4 to 20. However, for the linear model, the average deviations and SSE increase markedly when the number of training samples reduces. The optimum training sample number for the linear PLS model is 12 which is equal to the number of process modeling variables. Secondly, it is also observed in Fig. 3 that the prediction trend of the 20-lumped kinetics model is more accurate than that of the linear PLS model when the feedstock or operating conditions changes obviously (samples between 44 and 47). Furthermore, it is another advantage for the 20-lumped model to accurately forecast the trend of different carbon number aromatics yield, as shown in Fig. 4. On the other hand, it is well

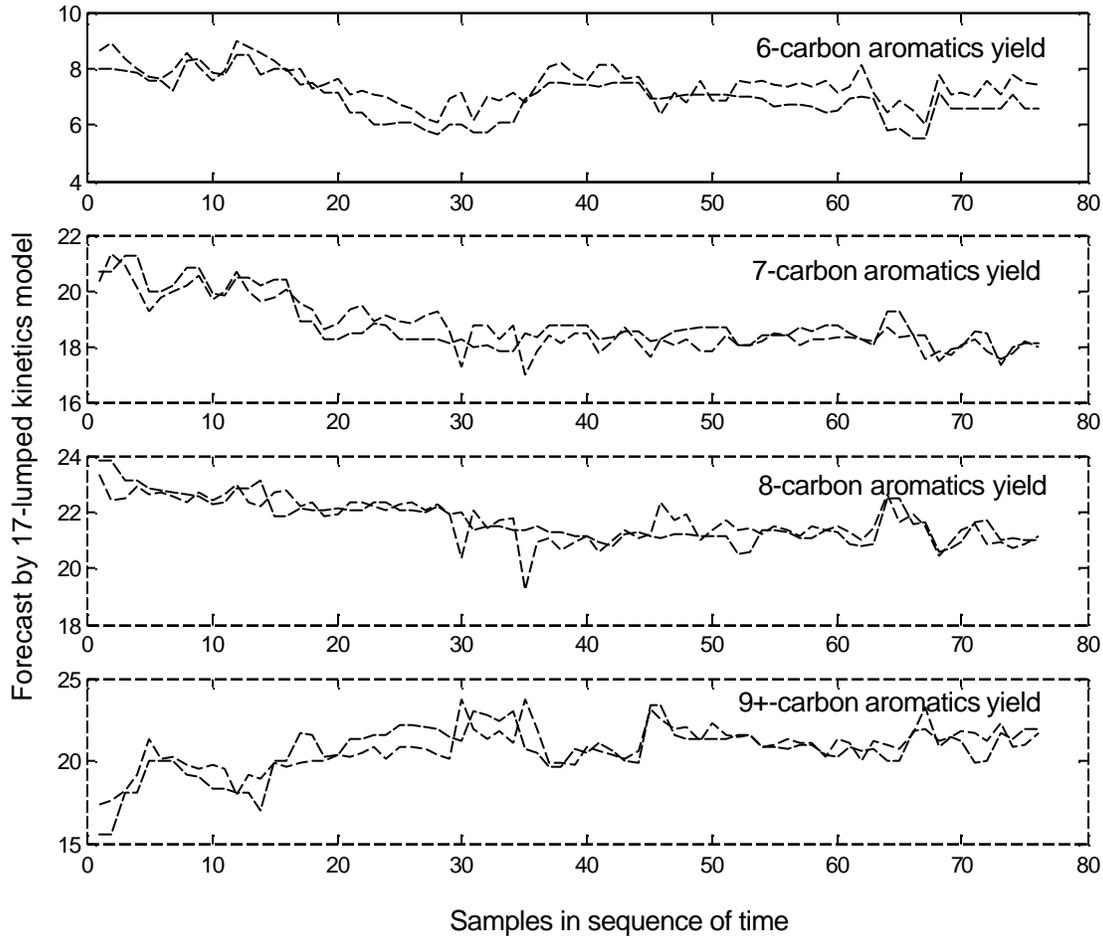


Fig. 4: On-line aromatics yield prediction precision of different carbon number by 20-lumped model (£-means the actual aromatics yield; means the predicted aromatics yield)

known that, in solving the model equations, the linear PLS model is quicker and more reliable than the kinetics model. Hence, the daily on-line prediction of aromatics yield can be carried out by the linear PLS regression model and it should be switched to the 20-lumped kinetics model when there are insufficient training samples, requirements of different carbon number aromatics yield or sudden and marked changes of feedstock or operating conditions.

A software package, named APC-sensor, including the two models and the on-line prediction and revision strategy mentioned in this section, has successfully been applied in the on-line aromatics yield prediction of the CCR process. The software package is proved to be reliable, stable and accurate. It can offer timely prediction result of the immeasurable aromatics yield to the operators and give them valid operating guidance; moreover, it can also provide on-line calculation of the immeasurable aromatics yield to the real-time advanced process control system so as to increase the control performance.

CONCLUSION

A 20-lumped kinetics model is simplified so as to increase the reliability and calculation speed. The off-line prediction performance of this simplified kinetics model is excellent. A simpler linear model including 12 process variables is proposed subsequently. Partial least squares (PLS) regression method is selected to estimate the linear model parameters. The off-line prediction performance of the linear PLS model is comparative with that of the kinetics model.

The two models are used to the on-line aromatics yield prediction for a CCR process. An on-line prediction and revision strategy is adopted. The average deviations between predicted and actual aromatics yield are 0.54 and 0.62%, respectively which is nearly equivalent to the off-line prediction performance. The difference between the two models is studied. A software package, named APC-sensor, including the two models, has successfully been applied in the CCR process.

NOMENCLATURE

C, P, N, A	=	Hydrocarbon, paraffins, naphthenes, aromatics
C_p	=	Specific heat, $\text{kJ kmol}^{-1} \text{K}^{-1}$
E_c	=	Activation energy, kJ mol^{-1}
F	=	Molar flow rate of oil gas in the furnace, kmol h^{-1}
H	=	Height of the catalyst bed, m
ΔH	=	Heat of reaction, kJ kmol^{-1}
k	=	Reaction rate coefficient, h^+
k_0	=	Frequency factor, $\text{sec}^{-1} \text{Mpa}^{-\theta}$
K_r	=	18×18 matrix for reaction rate coefficients
LHSV	=	Liquid hourly space velocity, h^+
P, Q	=	$n_x \times k$ and $n_r \times k$ burden matrices
r	=	Reaction rate, kmol sec^{-1}
R	=	Radius of catalyst bed, m
t_i and u_i	=	Score vectors
T	=	Reactor export temperature, K
V_c	=	Catalyst volume, m^3
y	=	Molar flow rate, kmol/h

Superscripts:

θ = Pressure exponent

Subscripts:

i = Reactor number or latent variable number
j = Lump or reaction number
1, ..., 9+ = Carbon atom number, 9+ means 9 and more

ACKNOWLEDGMENT

The authors would like to thank for the support by the National High Technology Research and Development Program (863 Program) of China (No. 2009AA043204, No. 2012AA040307).

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