

CHAPTER 5

PROCESS SIMULATION

5.1 Introduction

This chapter describes the development stages of the model. A kinetic scheme was proposed and used in this research based on very few researches. A derivation of the kinetic model was shown based on Langmuir-Hinshelwood kinetic model studies as presented in details in Chapter 2. The selection of the kinetic reaction model and the modeling of the reactor is Aspen Plus Simulation Package was made through the base case data obtained from TOC. The result shows a significant level of confidence of the model in correctly representing the process.

5.2 The Kinetic Reaction

In Aspen Plus, it provides a wide variety of reactions such as power law and user-defined kinetics models, generalized Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model for reactor models and Pressure-Relief. Researches (Schbib, (1996), Bos et al. (1993)) shows that a power rate law model could be developed from a Langmuir Hinshelwood theory. It is later used to predict the experiment studies compared with the power rate model. Due to difficulties in expressing hydrogenation rates using a Langmuir Hinshelwood model in Aspen, it was decided to incorporate the effects of surface interactions into a power law model by solving for a process determined the kinetic reaction rate, the pre-exponential value. All the reactions were assumed to be irreversible based on thermodynamic considerations

However, the power-law model cannot describe the rate of hydrogenation when the feeding pressure increases but this is not a concern since the operating pressure changes very little. The catalyst deactivation term was lumped with the pre-exponential factor, which allowed changes in model activity during the reaction period. Also, power

rate law used in this study did not predict a change in selectivity with CO content since laboratory results showed that the ratio of rate of acetylene hydrogenation to that of ethylene hydrogenation was dependant only on their concentrations. The lifetime of the catalyst for this plant is over three years on which the research focuses on the first year (1999) only.

As mentioned earlier, the power rate law reaction model in Aspen Plus Simulation Package was used, expression of the power rate law where the rate of reaction was calculated as the product of the reacting species concentrations with a rate constant representing the specific reactivity of the reaction. The kinetic rate expression in the segment-based model is described below:

$$\text{Rate} = \left(\prod_j C_j^{\alpha_{ij}} \right) k_{oi} e^{\frac{-Ea_i}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} \quad (5.1)$$

Where:

i	=	user reaction number
j	=	component number
Π	=	product operator
C_j	=	concentration of component j
α_{ij}	=	power law exponent for component j in reaction i
k_0	=	pre-exponential factor
Ea	=	activation energy (Mole-Enthalpy units)
b	=	temperature exponent
R	=	universal gas constant
T	=	temperature (Temperature units)
T_{ref}	=	optional reference (temperature units)

The power-law model for this reaction was based on a study conducted by Schbib, (1996) a detail of the mechanism and algorithm of the reaction is presented in Chapter 2. Each of the reactor holds and independent rate of reaction, thus in this study, a total of twelve reactions will be monitored and studied.

$$(-r_{C_2H_2}) = k_1 [C_2H_2]^0 [H_2]^1 \quad (5.2)$$

$$(-r_{C_2H_4}) = k_2[C_2H_4]^0[H_2]^{0.6} \quad (5.3)$$

$$(-r_{MA}) = k_3[C_3H_4]^0[H_2]^{-0.5} \quad (5.4)$$

$$(-r_{PD}) = k_4[C_3H_4]^0[H_2]^{-0.5} \quad (5.5)$$

Where

$$k_i = \text{pre-exponential factor}$$

5.3 Thermodynamic Properties

The thermodynamic property used in the simulation is Peng-Robinson. The reason is that the PENG-ROB method is suitable for non-polar or mildly polar mixtures. Examples are hydrocarbons and light gases such as carbon dioxide, hydrogen sulfide, and hydrogen. This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions. The coverage range gives reasonable results at all temperatures and pressures. The PENG-ROB method is consistent in the critical region. Therefore, it does not exhibit anomalous behavior, unlike the activity coefficient property methods. Simulation results from coefficient activity method are least accurate in the region near the mixture critical point.

5.4 Creation of The Model Based on Base Case

For this purpose, the model is constructed first by using the base case data. The focus point is at the actual plant layout of this section which is described as follows:

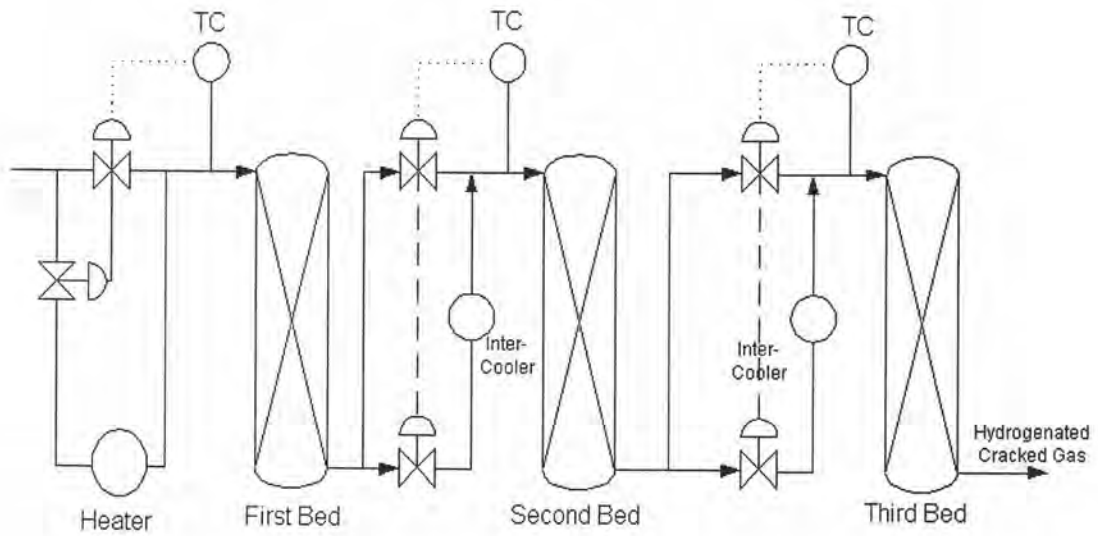


Figure 5.1 Actual equipment of acetylene hydrogenation unit

From figure 5.2, one can observe three major units, hence the reactor, six valves, and three heat exchangers.

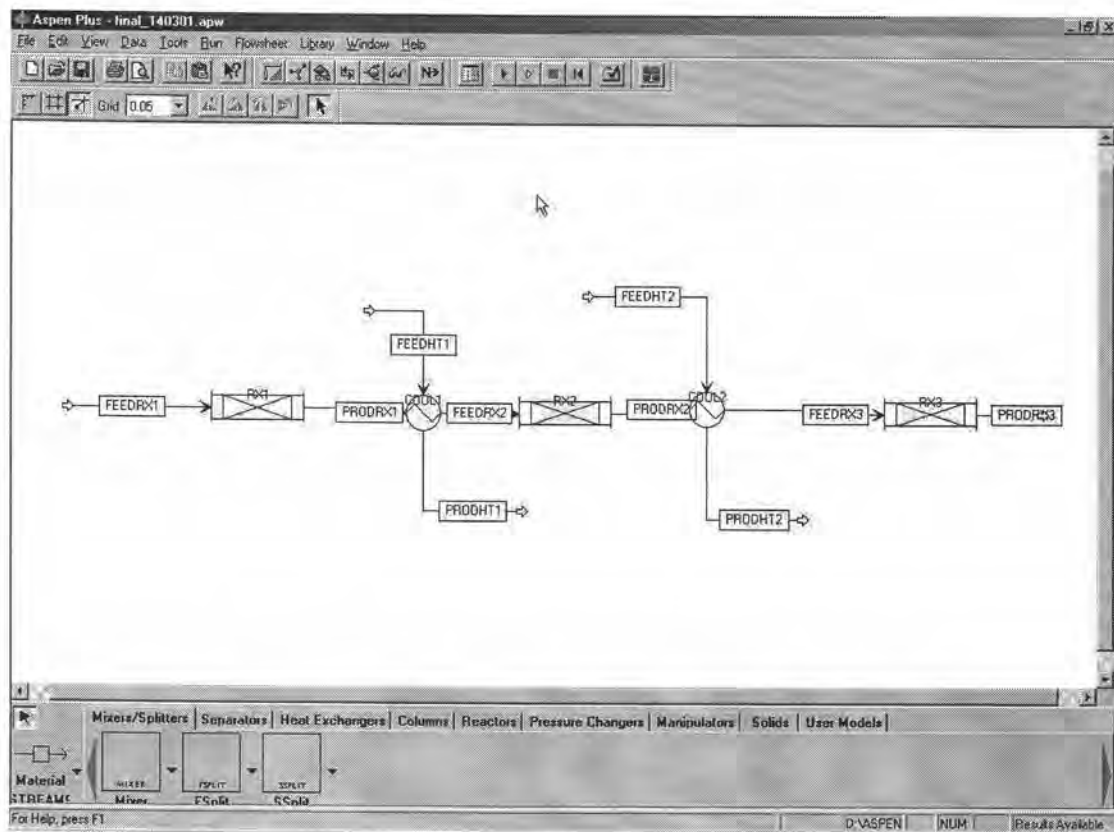


Figure 5.2 Simulation model of acetylene hydrogenation unit

In the simulation model, the set of inter-cooler valve is simplified into a heat exchanger due to its practicality, a temperature set point is given to the operator and then later will be keyed into the DCS. The DCS will automatically calculate the amount of by-pass flow ratios by itself.

The results of the simulation are described followed.

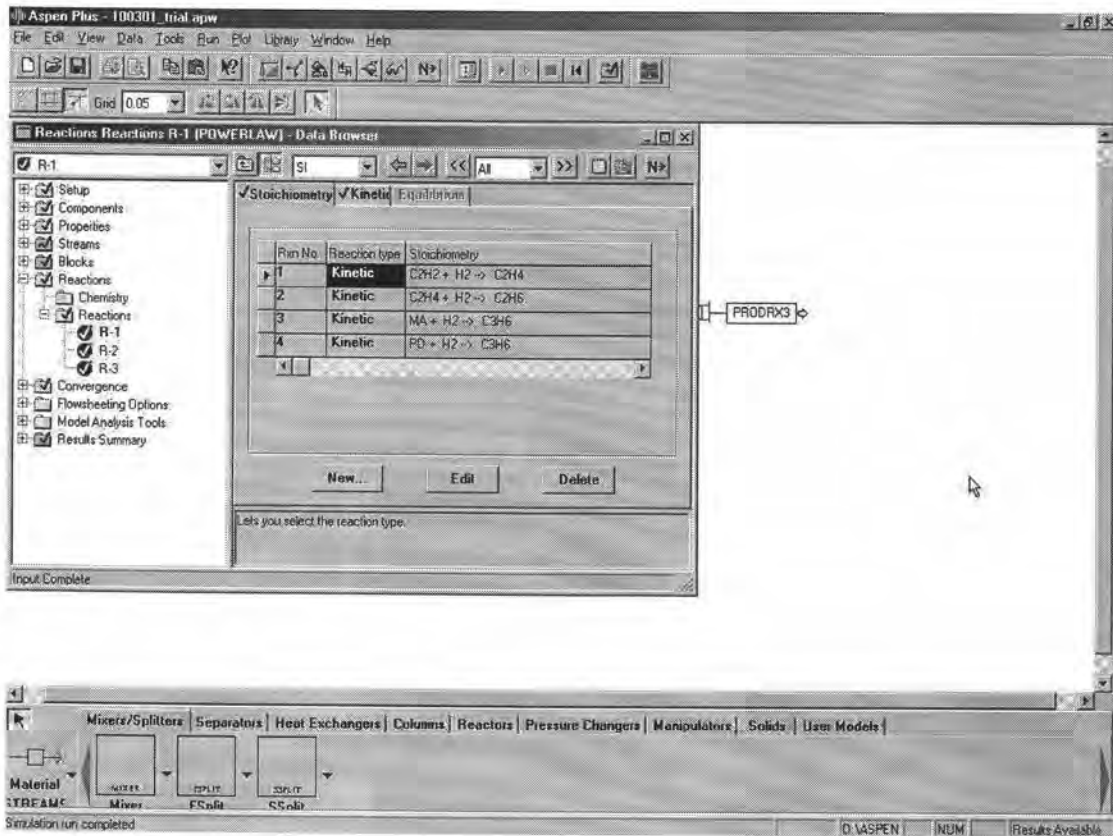


Figure 5.3 Entering the kinetic parameters for base case run

Table 5.1 The kinetic parameters for process simulation

Parameter	Initial value	Reactor 1	Reactor 2	Reactor 3
k_1	58.49	498.20	378.64	28.85
E_1 (kcal/mol)	9.00	9.00	9.00	9.00
k_2	1.47	45.36	80.03	601.59
E_2 (kcal/mol)	8.40	8.40	8.40	8.40
k_3	90.00	0.57	5021.05	3859.90
E_3 (kcal/mol)	12.60	12.60	12.60	12.60
k_4	90.00	0.15	1798.18	4105.70
E_4 (kcal/mol)	12.60	12.60	12.60	12.60

Initial values were obtained from Schbib et. al. (1996)

k_0 = pre-exponential factor

E_a = activation energy (Mole-Enthalpy units)

Table 5.2 Results from simulation for base case

Parameter	Design	Model	%Error
Temp (C)	126.00	127.50	1.19
H ₂ (kgmol/hr)	751.24	746.00	0.70
CO (kgmol/hr)	2.42	2.42	0.00
CH ₄ (kgmol/hr)	1382.80	1382.80	0.00
C ₂ H ₂ (kgmol/hr)	0.00	0.00	0.00
C ₂ H ₄ (kgmol/hr)	2089.50	2086.81	0.13
C ₂ H ₆ (kgmol/hr)	437.31	440.33	0.69
MA (kgmol/hr)	1.60	1.55	3.13
PD (kgmol/hr)	6.45	6.55	1.55
C ₃ H ₆ (kgmol/hr)	754.62	754.43	0.03

Note : %error = $\text{abs}(\text{design-simulate})/\text{design} * 100$

From Table 5.2, it is obvious that there is a significant relationship between the base case data and the simulated results. The results were all in an acceptable range. The

base case model provided would ease the fitting of the model to the actual plant data. The model also provides an understanding of the effect of pre-exponential and activation energy to the outlet temperature. Since this reactor is an exothermic reactor, the results of reaction causes a highly and dramatically change to the outlet temperature of each reactor. A outlet temperature of 126 °C should be taken in mind since it is considered high and could easily cause a runaway reaction.

This means that one could be confined with the model within a certain amount of confidence. The model still has a large amount of difference to the base case data due to that the kinetic reaction model pre-exponential factor was not correct and a trial and error was done roughly due to the limited availability of base case data. However, this model is not so important in terms of modeling, since vigorous model of the process will be constructed later with more actual process data, in which then one could fine tune the model to represent a more accurate perspective to the process.

5.5 Data Fit

Although the model created through theoretical kinetic fashion and base case data could be obtained, but its performance is still far different from the present condition of the plant. Thus it is necessary that the model be adjusted in order to represent the process at its current operation condition, and if possible, represent a wider range of operating period. Data fit was performed to fit the simulation model to match with the plant data.

Parameter regression usually involves adjusting model parameters to improve the agreement between model predictions and process data. For example, process rate constants may be manipulated to match the measured polymer molecular weight and monomer conversion. Manipulated parameters may include reaction rate or equilibrium constants, physical property constants, or equipment specifications. Fitted parameters may include model predictions such as reactant conversion, product yield, by-product content, polymer component attributes, stream compositions or flow rates, or equipment heat duty, temperature, pressure, or holdup. The data regression tool in Aspen Plus can be used to fit model parameters and reconcile process data. These applications may be carried out simultaneously.

The Data-Fit model can be used to reconcile input data and fit model parameters simultaneously. Simultaneous regression and reconciliation is typically used to fine-tune models which already match process data and trends relatively well. Data reconciliation runs involve manipulating one or more sets of model inputs to match model predictions to process data. For example, the average feed rate of a makeup stream can be estimated based on the flow rate and composition of the feed and product streams. Manipulated data typically includes feed stream flow rates and compositions, equipment operating conditions, heat transfer coefficients, etc. Data-Fit minimizes the weighted sum of squares of the differences between the measured data and the model prediction. In statistical terms, Data-Fit performs either ordinary least squares or maximum likelihood (errors-in-variables) estimation. Through the application of data reconciliation techniques, the level of process variable corruption due to measurement noise could be satisfactorily improved in a successive order.

The focused variables, F_i , P_i , T_i , and X_i , are considered temporally redundant since there are data formerly obtained from the process and considered stagnant. Since most of data are being sampled regularly and continuously at great frequencies, there was also data redundancy if the process conditions were at steady state. This is usually referred as “tempered redundancy”.

The X_i data were measured from the laboratory additionally for the online measurement, which can be categorized in the spatial redundant type.

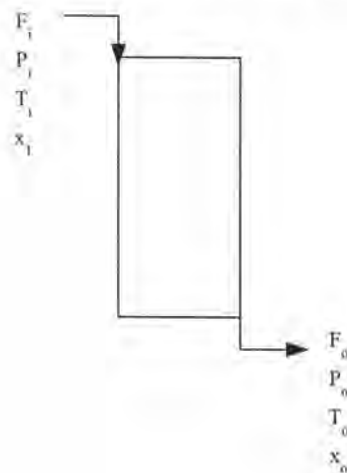


Figure 5.4 Data-Fit parameter selections

Whereas:

F_i = Feed flow rate (kg/hr)

F_o = Product flow rate (kg/hr)

T_i = Feed temperature ($^{\circ}\text{C}$)

T_o = Product temperature ($^{\circ}\text{C}$)

P_i = Feed pressure (kg/cm²)

P_o = Product pressure (kg/cm²)

X_i = Feed composition (mole fraction) (X refers to each component)

X_o = Product composition (mole fraction) (X refers to each component)

The interest was focused on the first reaction bed for data reconciliation as illustrated in Figure 5.4. In this study, Aspen Plus was used to determine the coefficient for kinetic model for each reaction in each reactor. Data was taken from both laboratory and online in a comprehensive data during March 1999 till December 1999.

A point-data data set type was used since:

- One or more steady-state experiments or operating points
- Initial charge and final products of a batch reactor, but not intermediate time points
- Feeds and products of a plug flow reactor, but not points along the length of the reactor

A stepwise approach is used to complete data reconciliation by using Aspen Plus. When data is fed, the specify these variables as follows:

Table 5.3 Variable definitions in Aspen Plus

Variables	Input as
Measured feed stream	Input
Measured product stream	Result
Measured variables that were accessed as input variables on the Define sheet	Input
All other measured variables	Result

Step 1: Development of the process model

A model made through the base case simulation was created earlier in the section 5.4. It will be valuable as a estimation tool used for data reconciliation in step 2.

Step 2: Development of the data reconciliation problem

The development of the data reconciliation was created in the form of an optimization problem. In general, the optimization step is not always straightforward. A manipulated variable was selected at this stage. A general rule of thumb to remember when using any sequential modular system is that only inlet stream property and process unit variables can act as manipulated variables. Inlet flow rate should always be chosen as manipulated variable when flow rate is being reconciled. Manipulations for obtaining the upper and lower limits for the manipulated variables were then determined. Determination of these limits would be based on several considerations including process knowledge and equipment restrictions. It is important that the final values of the manipulated variables do not lie on the bounds. If they do one should widen the bounds to allow the optimizer to find the unbounded optimum. The selected manipulated variables were F_i , P_i , T_i and X_i . The bounds were selected accordingly to the equipment specification such as the maximum pressure allowed or possible flow through pipe.

Step 3: Development of the objective function

The overall objective function is basically a sum of the squares of the variable mismatches divided by their variances and multiplied by a factor denoting the importance and/or confidence in the accuracy of the particular measurement. Created as a weight sum of squares of the adjustments of measured variables. The adjustment is defined as the difference between the adjusted and the measured values of the variables. The weights are normally the inverse of the corresponding variances evaluated as the sample variance of a set of measurement over a certain period of time at a steady state. The factor becomes larger as the variable becomes more important to match closely or its value is known more accurately. The temperature and concentration profiles of the acetylene hydrogenation reactor were carefully watched and focus by the plant engineers. Therefore, we set the weighting factor for temperature-measured data and

concentration profiles to be a high value, 10 and 1000 relative to the other weighting factors to force the optimizer to adjust other process variables instead. The other predefined factors provided by Aspen were reasonable enough; no changes has been made to it.

The objective function used in the simulation was as follows:

$$\begin{aligned}
 \text{Objective Function} = & 1/(\text{standard deviation of feed flow rate}) * (\text{feed flow rate} - F_i)^2 \\
 & + 1/(\text{standard deviation of feed pressure}) * (\text{feed pressure} - P_i)^2 \\
 & + 1/(\text{standard deviation of feed temperature}) * (\text{feed temperature} - T_i)^2 \\
 & + 1/(\text{standard deviation of feed concentration}) * \Sigma(\text{feed concentration} - X_i)^2 \\
 & + 1/(\text{standard deviation of product flow rate}) * (\text{product flow rate} - F_o)^2 \\
 & + 1/(\text{standard deviation of product pressure}) * (\text{product pressure} - P_o)^2 \\
 & + 1/(\text{standard deviation of product temp.}) * (\text{product temperature} - T_o)^2 \\
 & + 1/(\text{standard deviation of product conc.}) * \Sigma(\text{product concentration} - X_o)^2 \quad (5.45)
 \end{aligned}$$

Subjected to the constrains as follows:

1. The overall model balance equation and the component balance equation.

$$\begin{aligned}
 & [H2]_{in} + [CO]_{in} + [CH4]_{in} + [C2H6]_{in} + [C2H4]_{in} + \\
 & [C3H8]_{in} + [C3H6]_{in} + [C2H2]_{in} + [MA]_{in} + [PD]_{in} - 100 = 0 \quad (5.46)
 \end{aligned}$$

$$\begin{aligned}
 & [H2]_{out} + [CO]_{out} + [CH4]_{out} + [C2H6]_{out} + [C2H4]_{out} + \\
 & [C3H8]_{out} + [C3H6]_{out} + [C2H2]_{out} + [MA]_{out} + [PD]_{out} - 100 = 0 \quad (5.47)
 \end{aligned}$$

2. The overall energy balance equation

$$\begin{aligned}
 & [Cp_{\text{average}} * (\text{total mole}) * T]_{in} + \\
 & (\Delta Hr_{H2} * [H2]_{in} - [H2]_{out}) + (\Delta Hr_{CO} * [CO]_{in} - [CO]_{out}) + \\
 & (\Delta Hr_{CH4} * [CH4]_{in} - [CH4]_{out}) + (\Delta Hr_{C2H6} * [C2H6]_{in} - [C2H6]_{out}) +
 \end{aligned}$$

$$\begin{aligned}
 &(\Delta H_{r_{C_2H_4}} * [C_2H_4]_{in} - [C_2H_4]_{out}) + (\Delta H_{r_{C_3H_8}} * [C_3H_8]_{in} - [C_3H_8]_{out}) + \\
 &(\Delta H_{r_{C_3H_6}} * [C_3H_6]_{in} - [C_3H_6]_{out}) + (\Delta H_{r_{C_2H_2}} * [C_2H_2]_{in} - [C_2H_2]_{out}) + \\
 &(\Delta H_{r_{MA}} * [MA]_{in} - [MA]_{out}) + (\Delta H_{r_{PD}} * [PD]_{in} - [PD]_{out}) - Q = 0
 \end{aligned} \tag{5.48}$$

$$Q = [\text{Water flow rate} * C_{p_{H_2O}} * (T_{out} - T_{in})] \tag{5.49}$$

3. Heat transfer in the reactor and heat exchanger \leq Maximum Heat Transfer in each unit.

4. Minimum flow in pipe $\leq F_i \leq$ Maximum flow in pipe

Constraints 1 to 4 were automatically created in the Aspen Plus's reactor model.

Table 5.4 Result of data-fit for 31st April 1999 for lead bed

Lead Bed	Actual	Simulation	%Error
H2 (mol%)	0.1518715	0.1517971	0.0489775
CO (mol%)	0.0005716	0.0005734	0.3034420
CH4 (mol%)	0.2646988	0.2655408	0.3180841
C2H6 (mol%)	0.0827935	0.0822986	0.5977208
C2H4 (mol%)	0.3622089	0.3632158	0.2779711
C3H8 (mol%)	0.0042047	0.0042172	0.2954480
C3H6 (mol%)	0.1303472	0.1272070	2.4090912
C2H2 (mol%)	0.0004005	0.0015415	284.9324201
PD (mol%)	0.0019021	0.0020048	5.3982393
MA (mol%)	0.0010011	0.0016039	60.2059231
Temp (K)	352.40	352.60	0.0567537

$$\%Error = \text{abs}(\text{actual-simulate})/(\text{actual}) * 100$$

Table 5.5 Pre-exponent value for 31st April 1999 for lead bed

Pre-exponent	Value
K1	1077.40942
K2	214.518499
K3	1.32E-08
K4	1.34E-08

The result shows that most of the simulation results are within 1 or 2 % error, however, acetylene conversion was over predicted. A weight of 10 was added to the acetylene data fit term.

Table 5.6 Result of data-fit for 31st April 1999 for lead bed using weight = 10 for acetylene

Lead Bed	Actual	Simulation	%Error
H2 (mol%)	0.1518715	0.1517804	0.0599934
CO (mol%)	0.0005716	0.0005734	0.3051914
CH4 (mol%)	0.2646988	0.2655461	0.3200637
C2H6 (mol%)	0.0827935	0.0823002	0.5957521
C2H4 (mol%)	0.3622089	0.3632427	0.2853950
C3H8 (mol%)	0.0042047	0.0042173	0.2975884
C3H6 (mol%)	0.1303472	0.1272095	2.4071655
C2H2 (mol%)	0.0004005	0.0015218	280.0154776
PD (mol%)	0.0019021	0.0020049	5.4003422
MA (mol%)	0.0010011	0.0016039	60.2089197
Temp (K)	352.40	352.70	0.09

$$\%Error = \frac{\text{abs}(\text{actual}-\text{simulate})}{(\text{actual})} * 100$$

Table 5.7 Pre-exponent value for 31st April 1999 for lead bed using weight = 10 for acetylene

Pre-exponent	Value
K1	1011.94012
K2	0
K3	0
K4	0

Table 5.8 Result of data-fit for 31st April 1999 for lead bed using weight = 100 for acetylene

Lead Bed	Actual	Simulation	%Error
H2 (mol%)	0.1518715	0.1511705	0.4615238
CO (mol%)	0.0005716	0.0005738	0.3769142
CH4 (mol%)	0.2646988	0.2657370	0.3921872
C2H6 (mol%)	0.0827935	0.0823594	0.5242972
C2H4 (mol%)	0.3622089	0.3642227	0.5559764
C3H8 (mol%)	0.0042047	0.0042203	0.3696498
C3H6 (mol%)	0.1303472	0.1273009	2.3370067
C2H2 (mol%)	0.0004005	0.0008040	100.7605851
PD (mol%)	0.0019021	0.0020063	5.4760461
MA (mol%)	0.0010011	0.0016051	60.3237899
Temp (K)	352.40	355.10	0.77

$$\%Error = \frac{\text{abs}(\text{actual}-\text{simulate})}{(\text{actual})} * 100$$

Table 5.9 Pre-exponent value for 31st April 1999 for lead bed using weight = 100 for acetylene

Pre-exponent	Value
K1	1242.39963
K2	0
K3	0
K4	0

Table 5.10 Result of data-fit for 31st April 1999 for lead bed using weight = 1000 for acetylene

Lead Bed	Actual	Simulation	%Error
H2 (mol%)	0.1518715	0.1508395	0.6794844
CO (mol%)	0.0005716	0.0005740	0.4171489
CH4 (mol%)	0.2646988	0.2658406	0.4313374
C2H6 (mol%)	0.0827935	0.0823915	0.4855018
C2H4 (mol%)	0.3622089	0.3647548	0.7028585
C3H8 (mol%)	0.0042047	0.0042219	0.4086534
C3H6 (mol%)	0.1303472	0.1273506	2.2989161
C2H2 (mol%)	0.0004005	0.0004143	3.4530695
PD (mol%)	0.0019021	0.0020071	5.5175781
MA (mol%)	0.0010011	0.0016057	60.3867187
Temp (K)	352.40	356.40	1.14

$$\%Error = \frac{\text{abs}(\text{actual}-\text{simulate})}{(\text{actual})} * 100$$

Table 5.11 Pre-exponent value for 31st April 1999 for lead bed using weight = 1000 for acetylene

Pre-exponent	Value
K1	1320.62404
K2	0
K3	0
K4	0

The result was within a acceptable percentage and the same procedure was done to the intermediate bed and guard bed, the results is show in table 5.12 and 5.13 accordingly

Table 5.12 Result of data-fit for 31st April 1999 for Intermediate Bed

Intermediate Bed	Actual	0.0433	%error	0.00433	%error	0.000433	%error	0.0000433	%error
H2 (mol%)	0.1489533	0.1473882	1.0506872	0.1470250	1.2945422	0.1469928	1.3162000	0.1454211	2.3713564
CO (mol%)	0.0005716	0.0005763	0.8313391	0.0005766	0.8680788	0.0005766	0.8820749	0.0005777	1.0675231
CH4 (mol%)	0.2655733	0.2669110	0.5036934	0.2670103	0.5411181	0.2670449	0.5541202	0.2675369	0.7393948
C2H6 (mol%)	0.0846871	0.0847665	0.0936706	0.0852029	0.6090617	0.0853798	0.8179245	0.0874015	3.2051110
C2H4 (mol%)	0.3633739	0.3646284	0.3452307	0.3644050	0.2837541	0.3641081	0.2020586	0.3628048	0.1566188
C3H8 (mol%)	0.0042043	0.0042389	0.8230510	0.0042405	0.8606313	0.0042411	0.8737131	0.0042489	1.0594741
C3H6 (mol%)	0.1303341	0.1294305	0.6933210	0.1294461	0.6813134	0.1295264	0.6197102	0.1298532	0.3690007
C2H2 (mol%)	0.0002002	0.0000000	100.0000000	0.0000000	100.0000000	0.0001001	50.0164860	0.0002102	4.9668778
PD (mol%)	0.0017018	0.0014348	15.6886105	0.0012947	23.9218944	0.0012422	27.0040138	0.0015641	8.0887917
MA (mol%)	0.0004004	0.0006254	56.1941107	0.0007988	99.5020010	0.0007880	96.7972870	0.0003818	4.6607052
Temp (K)	361.05	358.70	0.6508794	359.69	0.376679	360.08	0.268661	364.80	1.038637
K1		544.868257		354.252314		94.2757604		57.6521739	
K2		135.169337		160.158242		171.9251		275.609846	
K3		4.61E+03		3722.35122		3796.53118		5000	
K4		2.71E+03		3298.63036		3561.98624		1846.60695	

Table 5.13 Result of data-fit for 31st April 1999 for Guard Bed

Guard Bed	Actual	weight = 0.090569	%error	Weight = 0.0090570	%error	weight = 0.00090571	%error	weight = 0.000090572	%error
H2 (mol%)	0.1423465	0.1444990	1.5122015	0.1445067	1.5175827	0.1445068	1.5176249	0.139476	2.0167725
CO (mol%)	0.0005716	0.0005783	1.1759928	0.0005783	1.1759928	0.0005783	1.1759928	0.000582	1.7708267
CH4 (mol%)	0.2689768	0.2678256	0.4279987	0.2678232	0.4288910	0.2678231	0.4288984	0.269397	0.1563268
C2H6 (mol%)	0.0890917	0.0879034	1.3337782	0.0878729	1.3680238	0.0878726	1.3683830	0.093838	5.3278094
C2H4 (mol%)	0.3626732	0.3629747	0.0831435	0.3630222	0.0962214	0.3630227	0.0963648	0.359713	0.8162199
C3H8 (mol%)	0.0043044	0.0042535	1.1841119	0.0042534	1.1850411	0.0042534	1.1850411	0.004278	0.6042441
C3H6 (mol%)	0.1304342	0.1304784	0.0338893	0.1304771	0.0328773	0.1304771	0.0328696	0.131669	0.9467939
C2H2 (mol%)	0.0000010	0.0000242	2324.6000000	0.0000033	230.4700000	0.0000031	206.4200000	0.000000	100.0000000
PD (mol%)	0.0014014	0.0013874	0.9998332	0.0013875	0.9941248	0.0013875	0.9941248	0.001046	25.3290584
MA (mol%)	0.0001001	0.0000754	24.6935701	0.0000755	24.6256401	0.0000755	24.6256401	0.000000	100.0000000
Temp (K)	349.91	350.10	0.0542997	350.10	0.054300	350.10	0.054300	349.40	0.145752
K1		66.452771		74.7206602		74.8074438		250.40546	
K2		31.6063566		29.3038879		29.2797201		614.76146	
K3		1.81E+03		1813.47407		1813.47376		4356.52083	
K4		1.05E+03		1054.01678		1054.0137		5000	

After obtaining the pre-exponent factors, a CSTR model of the process was studied to check the reactor model according to Sauro, 1998 that a catalytic fixed bed adiabatic reactor could be approximated by a series of continuous stirred tank reactor system.

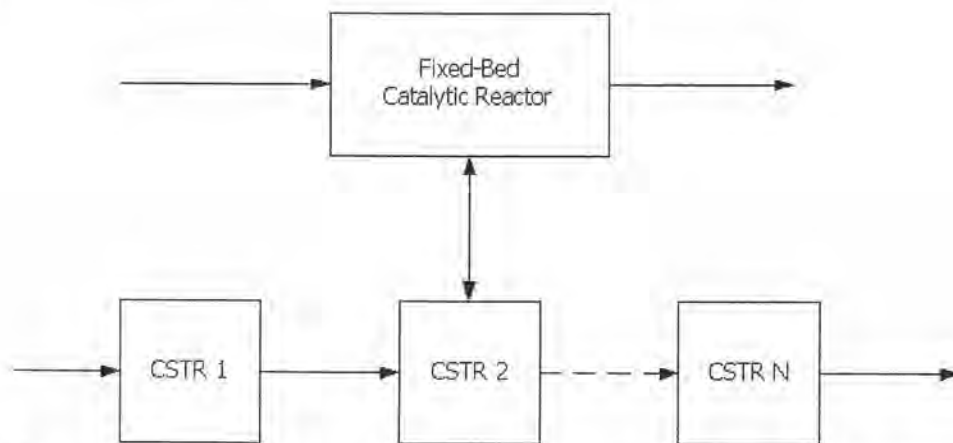


Figure 5.5 Similar-comparing between fixed-bed catalytic reactor and N number of CSTRs

As referred in chapter 2, it was mentioned that a number of n-CSTRs connected in series could represent a performance of a Plug Flow reactor. Each Plug flow reactor in this research has a volume of 10,758.38 liter, it was decided to represent this PFR with a number of 10 equal-volume reactor, 1,075.838 liter per CSTR. The result of the simulation is shown in table 5.14, 5.15 and 5.16.

Figure 5.6 to figure 5.11 shows the result of temperature and acetylene concentration of both the Plug flow reactor and 10 CSTRs, the 10 CSTR had the performance similar to the plug flow reactor. The result of the lumped parameter for both plug flow reactor and 10 CSTR are shown in table 5.17, 5.18 and 5.19. The result shows that the lumped parameters for both reactors are barely the same, however, the plug flow reactor still could performance and gives a better estimation than the CSTR.

The catalyst parameter was determined to enable the model to better fit to actual process. The result is shown in figure 5.12. Significant decrease in the catalyst activity could be notice, a drop of performance from 1 to 0.86 within 6 months. However, to compensate with the decrease of catalyst activity, an temperature and CO concentration was increased to maintain the level of activity as carried out in literature review in chapter 2.

Table 5.14 Composition comparison for 10 CSTRs in series for lead bed

Lead Bed	Actual	10 CSTRs
H2 (mol%)	0.15129395	0.15356767
CO (mol%)	0.00037924	0.00038074
CH4 (mol%)	0.25655932	0.25444838
C2H6 (mol%)	0.08555313	0.08515031
C2H4 (mol%)	0.37163078	0.37159441
C3H8 (mol%)	0.00400249	0.00401944
C3H6 (mol%)	0.12737910	0.12702377
C2H2 (mol%)	0.00050031	0.00049906
PD (mol%)	0.00170106	0.00180930
MA (mol%)	0.00100062	0.00150691
Temp (K)	351.87	356.82218

Table 5.15 Composition comparison for 10 CSTRs in series for intermediate bed

Intermediate Bed	Actual	10 CSTRs
H2 (mol%)	0.1478741	0.1509943
CO (mol%)	0.0003792	0.0003819
CH4 (mol%)	0.2577291	0.2552220
C2H6 (mol%)	0.0849426	0.0865850
C2H4 (mol%)	0.3732870	0.3718124
C3H8 (mol%)	0.0041021	0.0040317
C3H6 (mol%)	0.1298651	0.1290103
C2H2 (mol%)	0.0000200	0.0000236
PD (mol%)	0.0015008	0.0014759
MA (mol%)	0.0003002	0.0002500
Temp (K)	358.95	362.22

Table 5.16 Composition comparison for 10 CSTRs in series for guard bed

Guard Bed	Actual	10 CSTRs
H ₂ (mol%)	0.1448897	0.1456535
CO (mol%)	0.0003792	0.0003748
CH ₄ (mol%)	0.2582599	0.2544968
C ₂ H ₆ (mol%)	0.0922571	0.0922094
C ₂ H ₄ (mol%)	0.3689284	0.3691834
C ₃ H ₈ (mol%)	0.0042026	0.0041518
C ₃ H ₆ (mol%)	0.1298804	0.1301331
C ₂ H ₂ (mol%)	0.0000010	0.0000010
PD (mol%)	0.0012007	0.0012011
MA (mol%)	0.0000008	0.0000551
Temp (K)	347.00	348.06

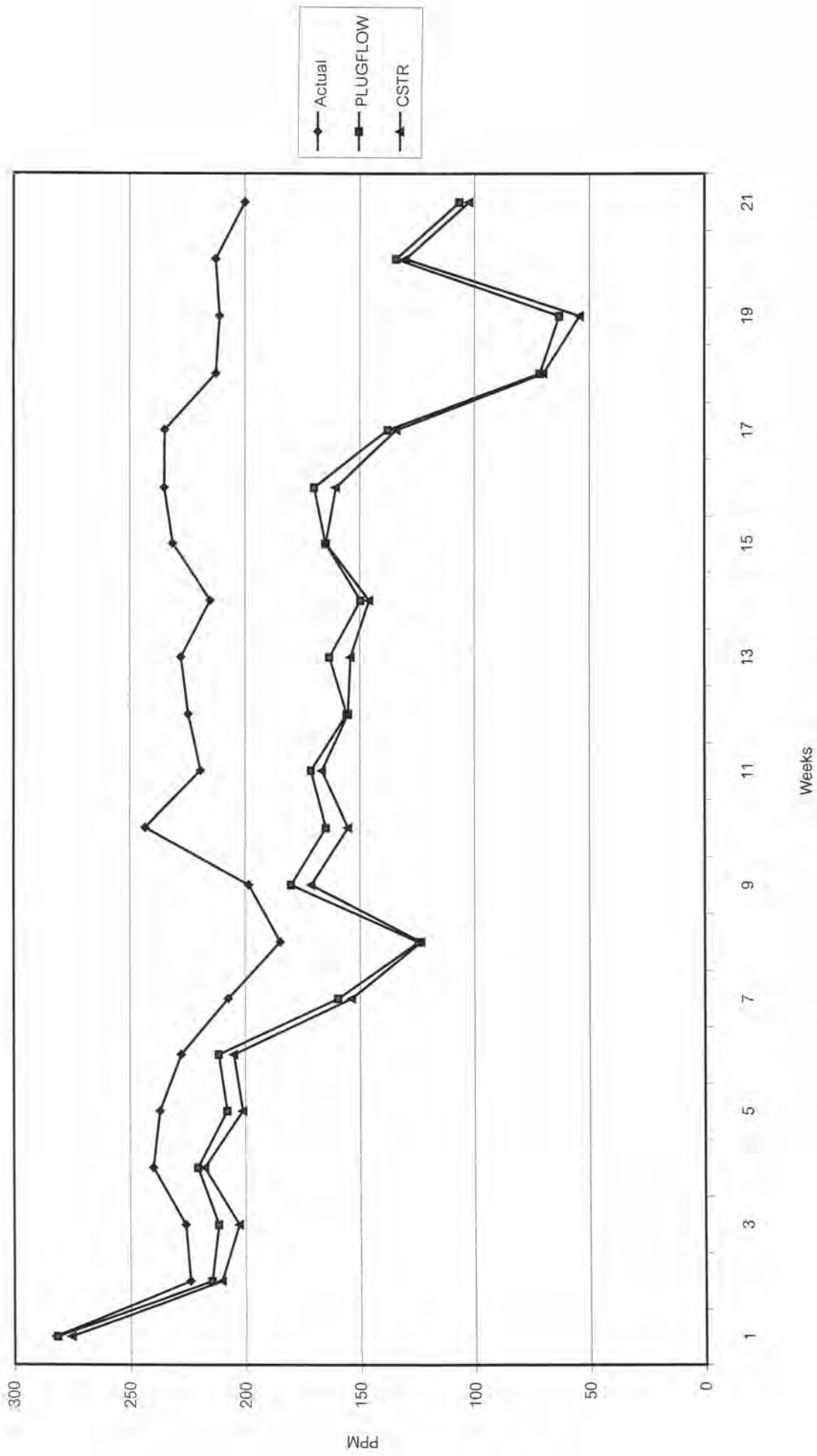


Figure 5.6 Acetylene fraction estimated result for lead bed

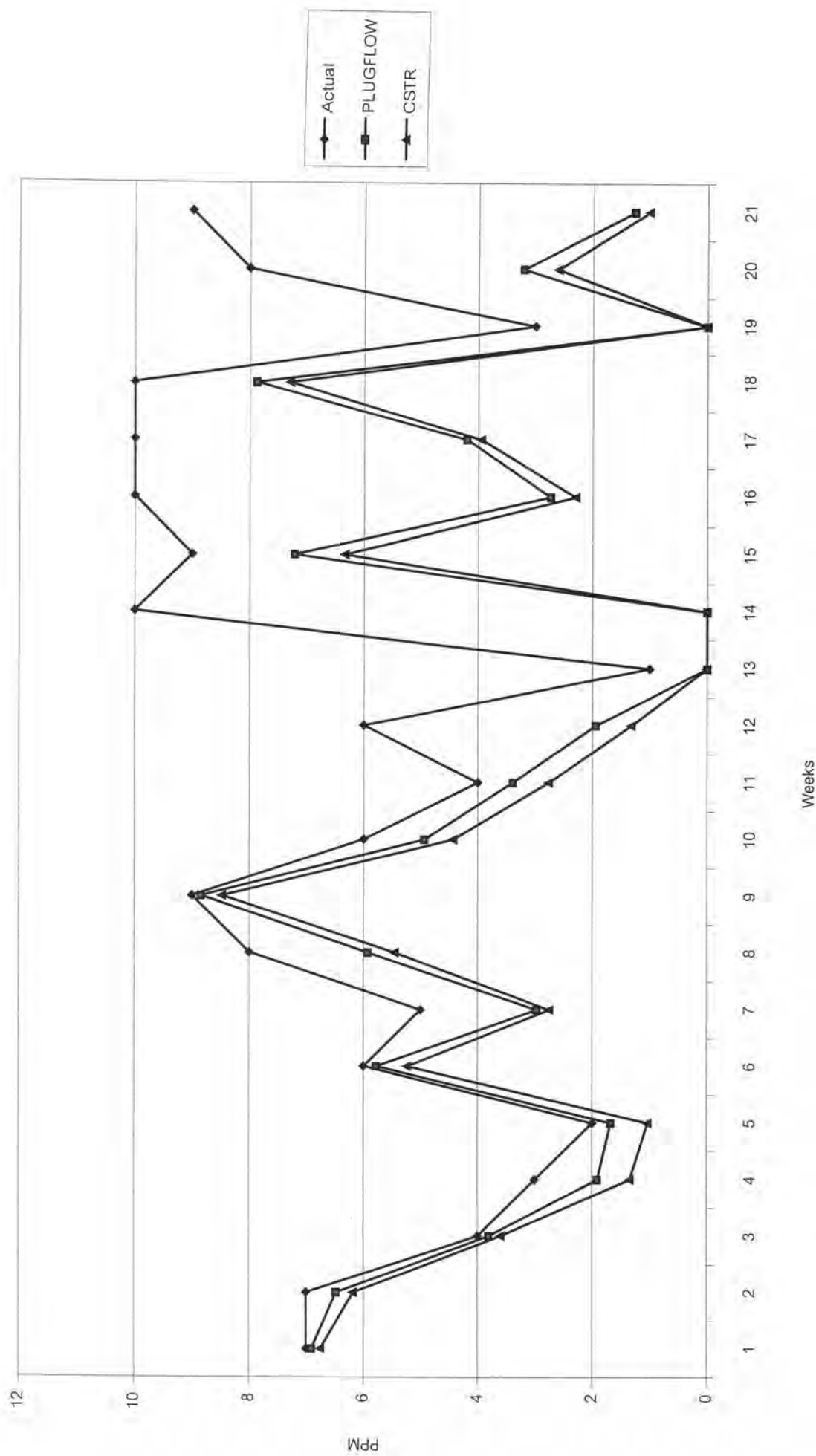


Figure 5.7 Acetylene fraction estimated result for intermediate bed

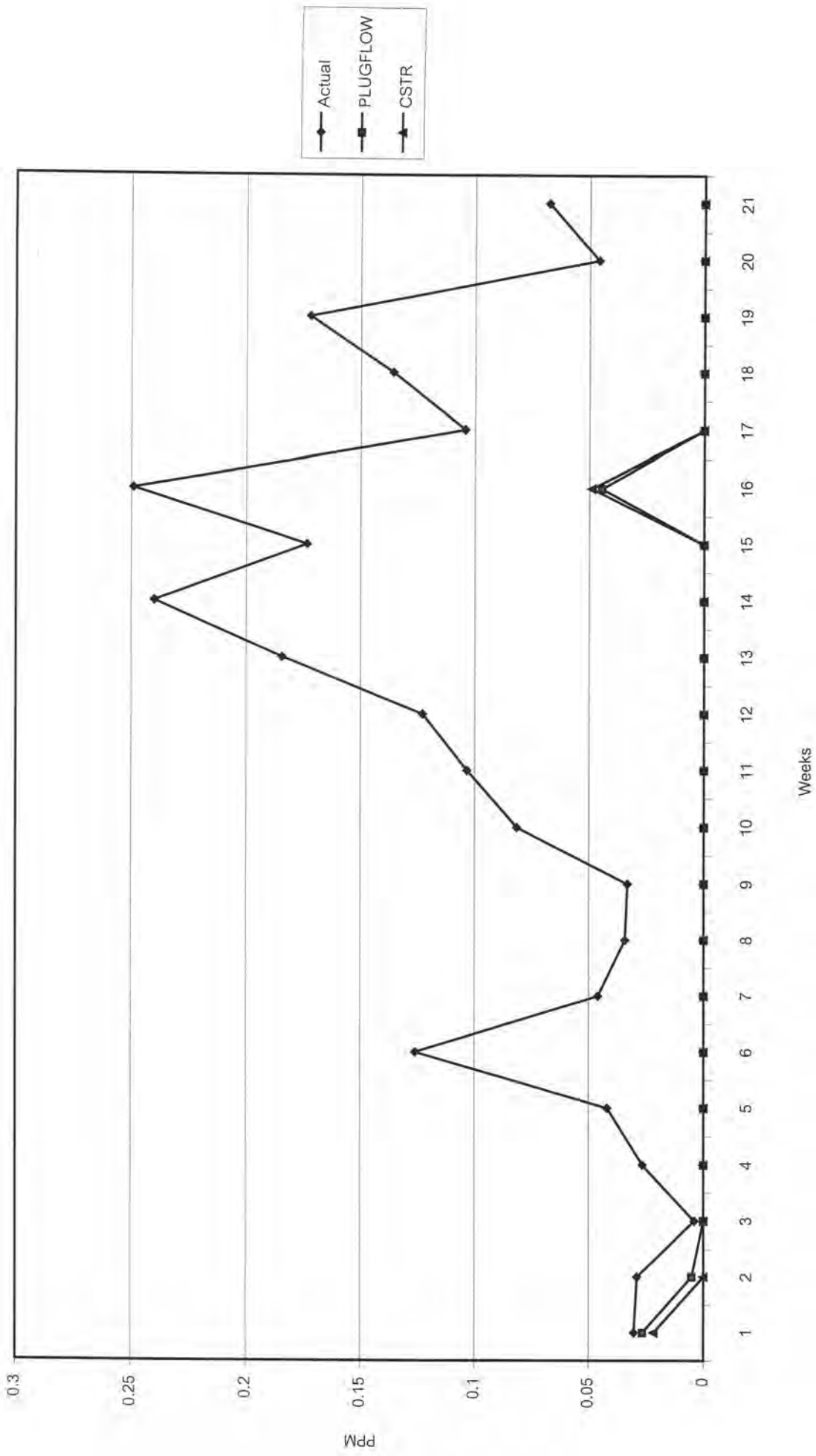


Figure 5.8 Acetylene fraction estimated result for guard bed

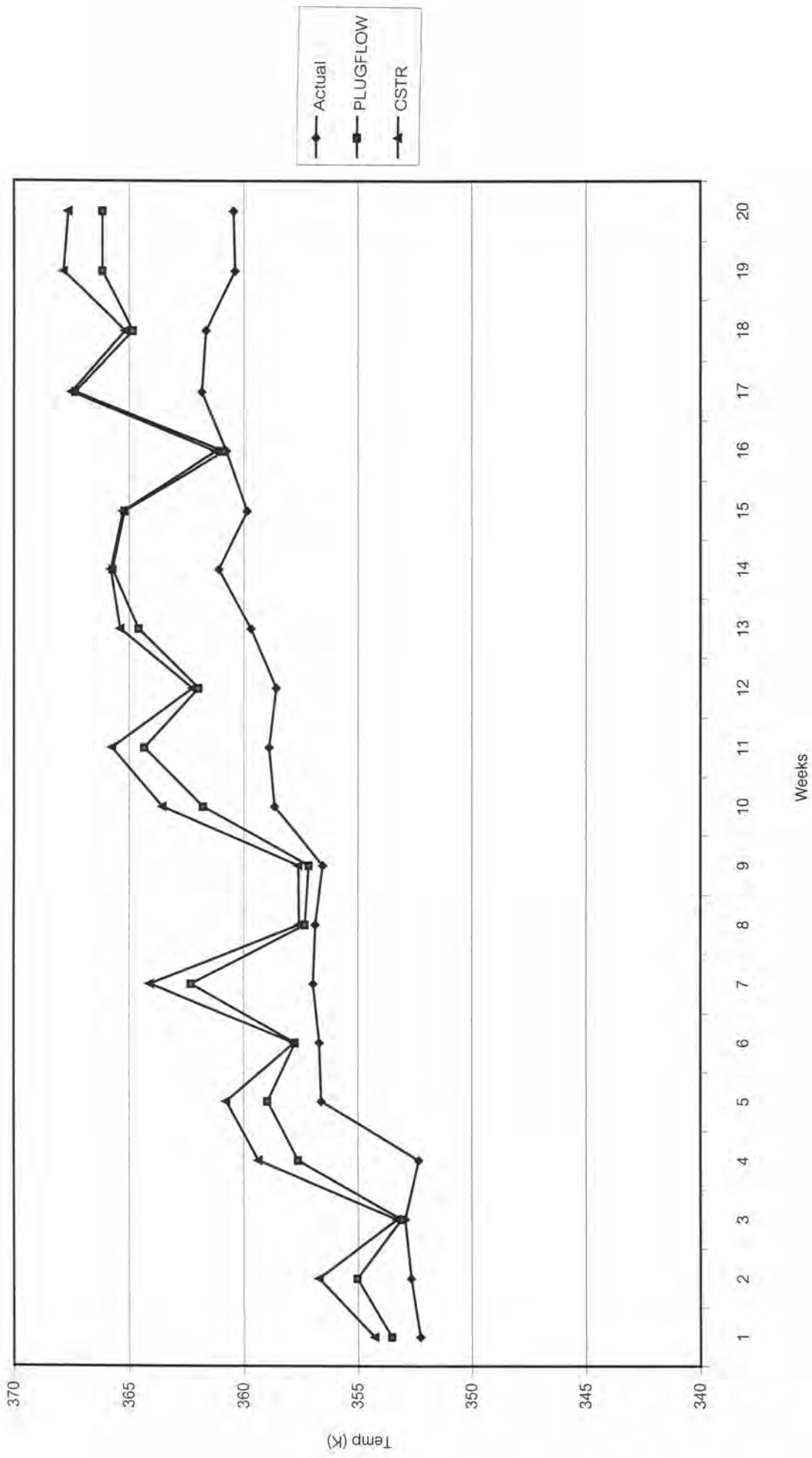


Figure 5.9 Temperature estimation from lead bed

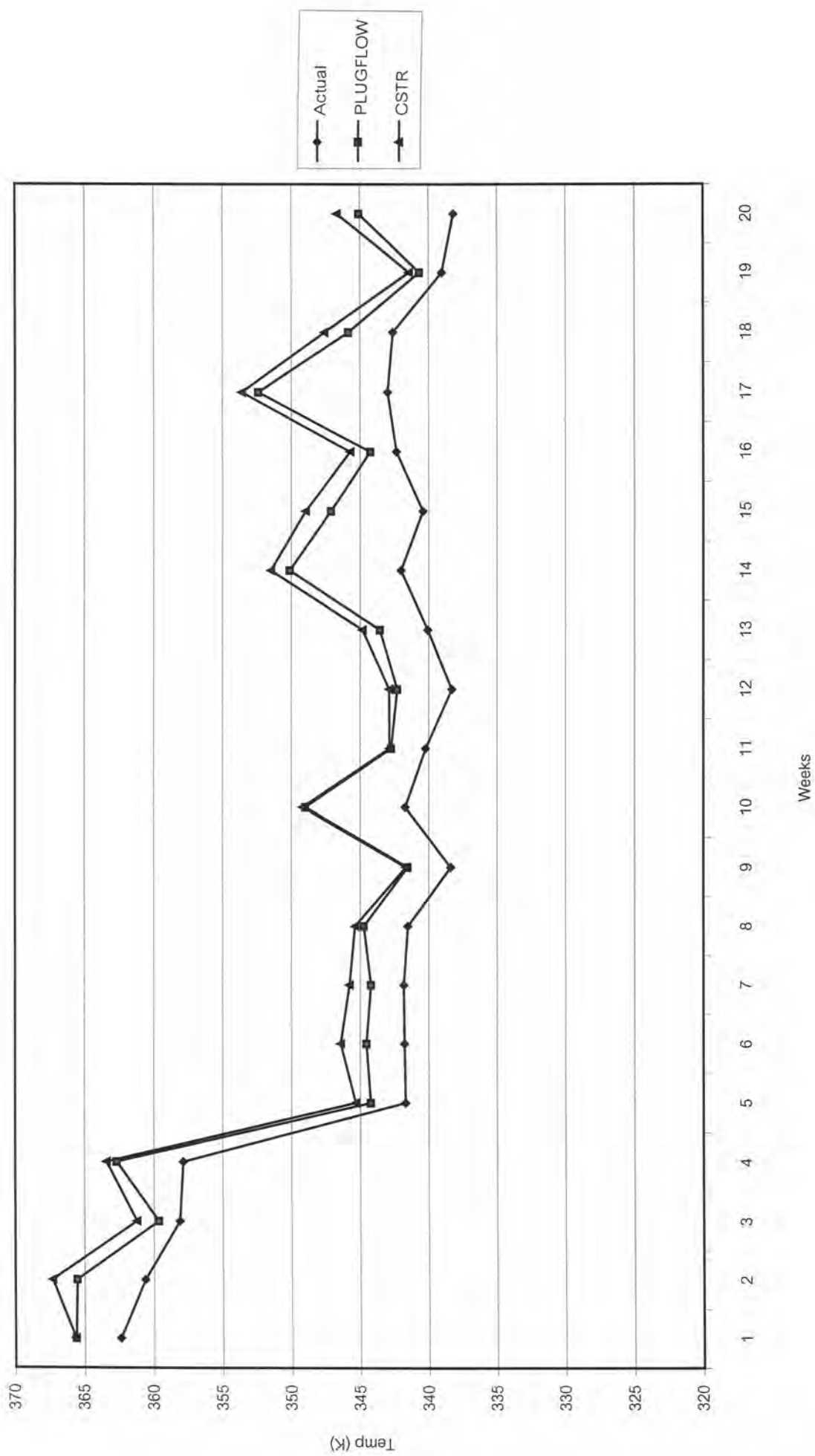


Figure 5.10 Temperature estimation from intermediate bed

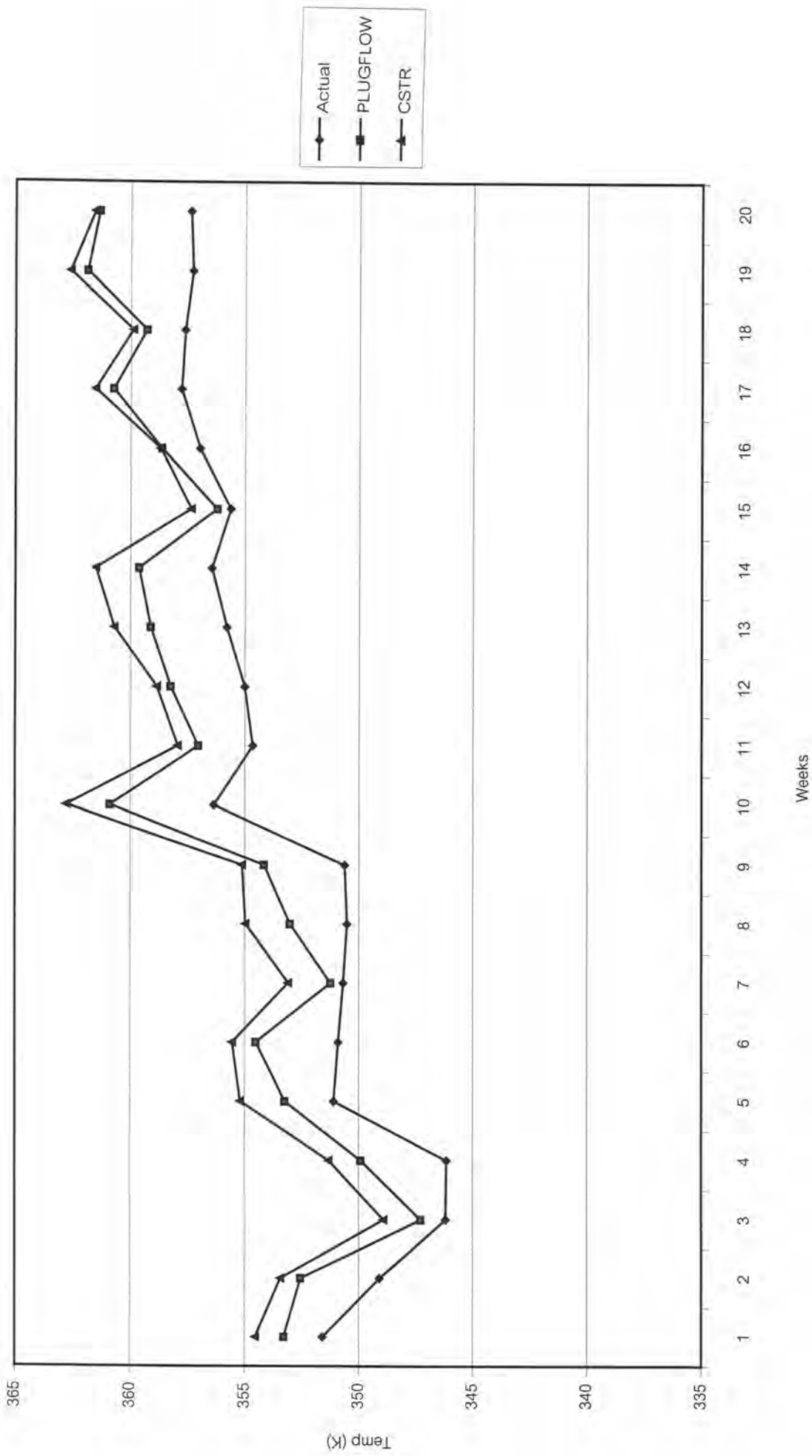


Figure 5.11 Temperature estimation from guard bed

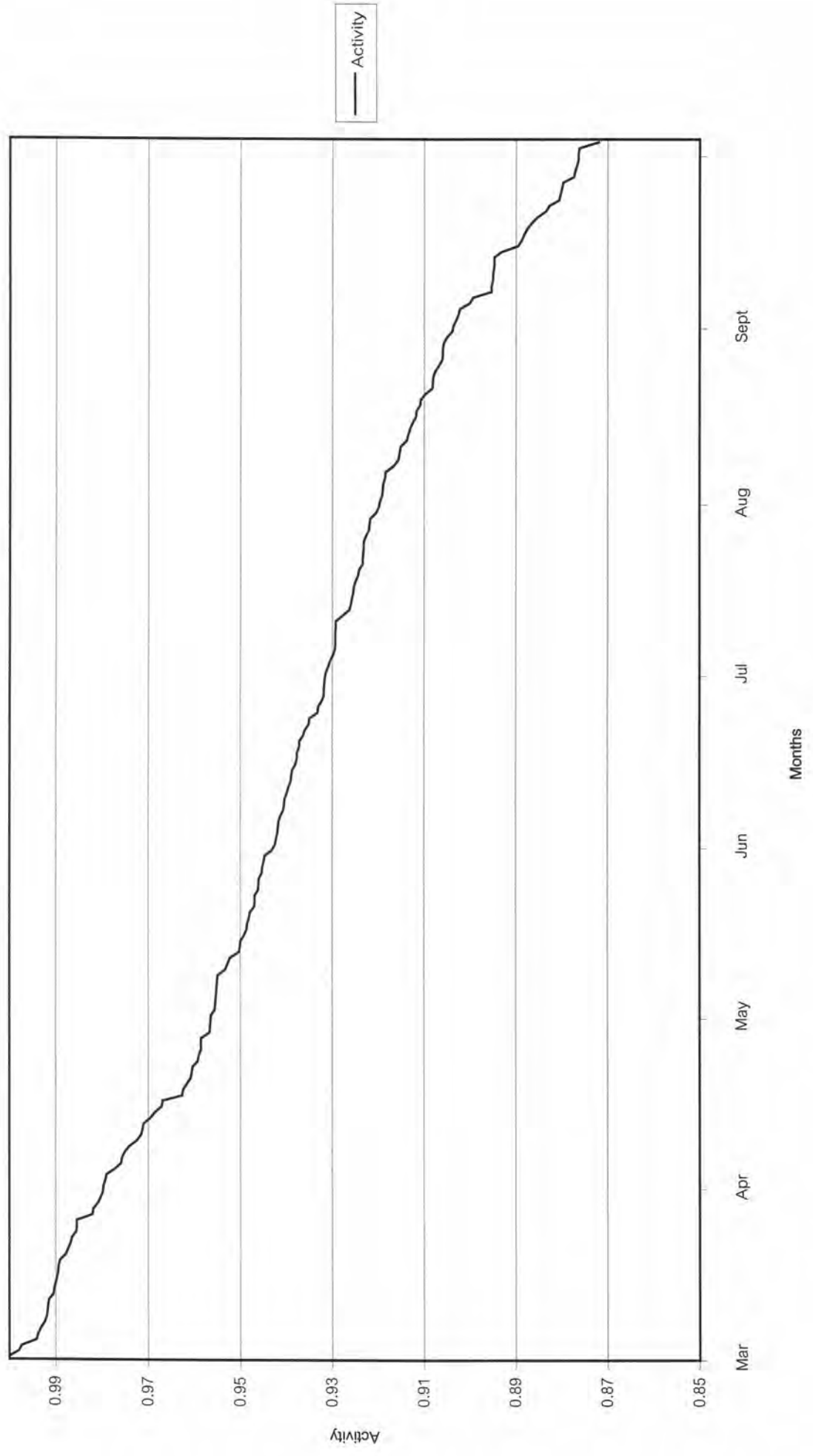


Figure 5.12 Catalyst Activity

Table 5.17 Values of lumped parameter for each reaction for lead reactor

	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
K1	1249.21	1160.39	1243.20	1134.15	1120.65	1206.62	1236.71	1193.39	1167.87	1182.24
K2	1345.68	1203.05	1195.54	1204.01	1159.91	1187.66	1175.94	1175.09	1169.23	1187.13
K2	45.36	40.53	40.15	41.96	34.00	37.14	42.66	40.06	33.09	42.25
K2	65.48	58.64	44.25	40.24	78.46	44.38	40.82	41.00	39.29	30.17
K3	0.88	0.22	0.62	0.35	0.00	0.50	0.75	0.00	0.00	0.24
K3	3.15	0.16	0.59	4.84	5.64	3.15	0.81	0.33	0.00	0.06
K4	0.24	0.18	0.18	0.21	0.13	0.20	0.20	0.15	0.18	0.14
K4	0.00	0.00	0.19	0.18	0.12	0.17	0.00	0.00	0.00	0.20

Table 5.18 Values of lumped parameter for each reaction for intermediate reactor

	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
K1	155.79	148.66	127.15	146.43	116.81	122.89	135.06	137.62	140.95	114.19
K1	168.46	106.68	138.08	149.45	118.24	114.02	138.85	130.94	131.11	138.33
K2	86.16	177.46	83.94	183.67	74.43	85.15	145.76	65.26	252.21	284.33
K2	93.45	78.70	83.35	65.99	94.81	135.05	284.40	84.20	183.15	184.43
K3	7051.71	6906.00	6848.10	6794.66	6850.62	7022.10	6836.56	6734.67	6625.44	6652.14
K3	7315.99	6675.71	6786.65	6885.43	6914.17	6767.85	6724.10	7048.54	7013.30	6606.60
K4	1894.31	982.58	1698.20	1644.66	1509.15	1711.89	1477.76	1740.53	1514.23	1641.84
K4	2405.15	2685.60	3548.00	2863.43	1594.96	1692.91	1595.81	1510.60	1792.15	1600.34

Table 5.19 Values of lumped parameter for each reaction for guard reactor

	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
K1	9.76	4.14	5.85	1.98	9.10	0.00	0.00	4.46	0.48	0.00
K1	8.54	2.61	3.33	7.49	0.00	0.00	0.00	0.00	6.63	8.62
K2	600.68	582.80	516.27	546.28	590.75	722.10	657.12	644.89	602.23	616.40
K2	468.40	508.38	441.29	565.28	584.78	773.78	634.20	699.02	593.61	618.55
K3	2358.47	2232.74	1509.60	2011.73	1677.51	471.78	653.62	1873.03	1701.35	2024.19
K3	2648.40	1784.05	1584.51	1497.04	1931.10	520.58	1959.52	2349.84	654.85	685.15
K4	3903.46	2940.51	3063.09	3386.55	2980.38	2567.18	3799.64	2182.80	2945.21	2696.57
K4	4684.80	3287.18	3290.49	3809.62	3005.94	2946.37	3879.74	3563.19	3368.24	2892.86

5.6 Summary

In this chapter, a model was created from base case. The result shows that the effluent temperature wrong and the design model was operating over the maximum allowed temperature outlet, 100 °C, which would easily lead to a runaway reaction since the reactions in the acetylene hydrogenation unit are all exothermic. The data of the base case model was also insufficient providing only the inlet and outlet profile from the unit, the data between the reactors were not provided making the model very flexible.

After the base case model was created, the model was then taken into the data fit and data reconciliation stage. The results observed give a good overview of the actual process. The first reactor removes about 80% to 95% of the total acetylene leaving the a minority of 5% 20% for the second reactor. The model is able to predict the slight loss of ethylene in the lead reactor. The result was confirm with the information from operations that the first bed was the most active bed leading the best acetylene conversion compared to the others.

The intermediate bed eliminates almost all of the acetylene, with a lower conversion rate of acetylene to ethylene. The conversion of ethylene to ethane starts at this reactor after the concentration of acetylene decreases to level of 10-100ppm. This supports the two site theory of Langmuir-Hinshelwood kinetic concept. Moreover, the methyl-acetylene and propadiene conversion starts at this reactor. The model was unable

to predict the loss of them within a reasonable error, due to limited reaction knowledge in literature review for front-end acetylene hydrogenation unit.

The guard reactor model predicts a complete acetylene conversion, the modeled effluent concentration is within the acceptable process range. The larger errors observed in the guard bed profile are due to the inability of the model to predict total ethylene, methyl-acetylene and propadiene conversion.

Weighting used in the data fit experiment was made on acetylene, ethylene, ethane, methyl-acetylene and propadiene. The results shows that a weight of 1000 applied to acetylene offered a good prediction of the pre-exponent values for all of the three reactors, while a weight of 10 applied to ethane results a better prediction. Supporting the idea that the precision of the mole fraction of acetylene should be weighted equally with other mole fractions. A better fitting could also be done, considering that the mole fraction of the entire component is at the same equivalent precision level.

A 10 CSTR connected in series model was studied to evaluate the equivalent of nCSTRs model to the Plug flow model. The result shown that 10 CSTRs connected in series could represent the single plug flow reactor within a small range of difference.

Then, both of the models were tested with other sets of data to study the consistency and accuracy of the model along the operation period. The result shows the error increases as the model is used along the weeks, supporting the theory that the activity of the catalyst decreases that related to the fouling of active sites. Since the catalyst deactivation term is based on the pre-exponent term, the study of the pre-exponent term over the weeks was then observed. Another conclusion was that the plug flow model provides a slightly closer prediction to the actual plant than the CSTR model. An equivalent of result and trend could lead to a conclusion that the CSTR model performance was similar to the plug flow model.

The result of the study shows that the pre-exponent factor of all the reaction decreases along the weeks of the operation. Providing information to the user that the model should be updated on a monthly basis to correct the pre-exponent factor. A catalyst deactivation profile was made in order to study catalyst deactivation separately. Significant decrease, almost twenty percent, could be notice in a period of 6 months.

However, the results show that even if the effluent was almost correct, the predicted temperature was incorrect, an average of 4-8 degrees over estimate and

increasingly trend for the rest of the set months. This happened from an over prediction of the acetylene hydrogenation over time. A better temperature prediction could happen if the prediction of the acetylene hydrogenation could be made.

A study of the activation energy of all of the reaction was made to check the possibilities. The lowest activation energy was used for all of the reaction and still the temperature result was over estimated. A more rigorous kinetic model could be used to solve this problem of which till date this kinetic model used in this research was the closest to the operation in a TOC. A notice of this over estimated outlet temperature should be taken when using this model to predict the effluent temperature profile.