



## Estimation of Kinetic Parameters of Naphtha Lump Feeds

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### ABSTRACT

This Research thrives to evolve a technique to estimate kinetic parameters of naphtha lump-feed. Steady state material and energy balance models were developed from first principles on the mole fractions of feeds and temperature. The research focused to minimize the objective function  $S$  used to search for optimum kinetic parameters of the feeds. The achieved optimum parameters were used to solve for optimum yields of the products. The results of the activation energies and Arrhenius constants are stated explicitly as  $E_i$  354950 KJ/Kmol; 173566 KJ/Kmol; 395001 KJ/Kmol and 394005 KJ/Kmol, and  $A_i$ : 3.5445E12, 1.30E08, 3.212E18 and 5.414E18 of P, N, A & G species respectively. The optimal  $E_i$ -values and  $A_i$ - values gave calculated  $k_i$ -values of 5.63E-12; 2.46E-04; 1.76E-08 and 1.56E-08 of P, N, A & G. The results compared with the plant data gave deviations of:  $E_i$  0.424%, 0.535%, 0.0157% and 0.0951%;  $A_i$  15%, 9%, 30% and 18%, and  $k_i$  0.570%, 0.361%, 0.650% and 12% for the P, N, A, & G respectively. Other deviations compared with optimal yields, steady state yields and literature data gave results which show that the research work is of importance and best fit for estimating kinetic parameters of any hydrocarbon feeds.

**Key words:** Kinetic Parameters, Optimization, Activation Energies, Rate constant, objectives function, regression analysis

### 1. INTRODUCTION

Constrain optimization is the process of optimizing an objective function with respect to some variables in the presence of constraints on those functions or energy function (here is functions of activation energies in 5-lump kinetic models) which is to be minimized or a reward function or utility function to be maximized [1].

Constraints can be either hard constraints which set conditions for the variables that are required to be satisfied, or soft constraints which have some variable values that are penalized in the objective function if, and based on the extent that, the conditions on the variables are not satisfied [2].

Optimization is the use of specific methods to determine the most cost effective and efficient solution to a problem or design for a process. The technique is one of the major quantitative tools in industrial decision making. Optimization pervades the field of science engineering, and business. Optimization in chemical engineering process design or reactor design and models, is concerned with selecting the best among the entire set by efficient quantitative methods. Computers and associated software make the necessary computations feasible and cost-effective.

Kinetic parameters estimation is paramount because most Chemical reactions results in semi or final products formation which are essential for consumption. Industries that produce these products take into consideration the easy, cheap and best routes to maximize profits and satisfy consumers. The rate expressions of most of the reactions which are both/either simple and or complex reactions have major challenges as how the rate constants (forward and backward) can be gotten or calculated. Often activation energies and pre-exponential factors are the parameters to be estimated as they are the driving force of most successful reactions that give best yields. Thus this research considers the estimation of activation energies and pre-exponential factors of naphtha reforming reactor using lumped kinetic scheme.

The aim of this research is to estimate the kinetic parameters of the Naphtha Reforming reactor using lumped kinetic scheme.

The research is useful as: to achieve better route of optimization of kinetic parameters of most complex or simple reactions processes taking place in Refineries and Pharmaceutical industries.

Several authors have carried out estimation of kinetic parameters. Wordu [3] researched on dynamic simulation of industrial reformer (DSIRR) in which the research considers the estimation of kinetic parameters of Nigeria Reformer Naphtha feed. Erick & Gustavo [4] researched on Estimation of activation Energies using hydrodesulphurization of middle distillates. The Hydrodesulphurization (HDS) of different petroleum distillates was carried out in a batch reactor using commercial cobalt-molybdenum (CoMo) catalyst and reaction condition similar to industrial practice

Dolan, et al, [5] researched on the use of nonlinear regression technique to estimate kinetic parameters. The non linear models developed were numerically integrated using mat lab and which were further subjected to regression analysis to compute the kinetic rate constant and activation energies.

Periago, et al [6] carried out the study of kinetic parameters of *Bacillus stearothermophilus* spores under isothermal and non-isothermal heating conditions. The result indicates that it is easy and clearer to use 90% confidence interval of nonlinear regression to obtain good estimate of kinetic parameters (activation bores for process, 7°C and 8°C were applicable for isothermal and non isothermal conditions to achieve the estimates).

Mishra, et al. [7] researched on the bootstrap confidence intervals for the kinetic parameters of degradation of authocyamins in grape Pomace, where rate constant,  $k_r$  and activation energy ( $E_a$ ) for the degradation process were estimated at 113.9°C with initials  $k_r = 0.0606/\text{min}$  and  $E_a = 65.32\text{KJ/mol}$  and gave values asymptotic confidence levels and bootstrap confidence of 95% respectively for  $k_{113.9^\circ\text{C}}$  and  $E_a$  to be 0.052 and 0.068, and 23.3 and 102.7°C and 0.053 and 0.066, and 49.08°C and 104.9°C respectively.

Sulaiman, et al (2013) researched on the simultaneous and sequential estimation of kinetic parameters in a starch viscosity model. After studying the gelatinizing behavior of native corn starch, the kinetic parameters were estimated ( $k_r$  &  $E_a$ ) both by ordinary least squares and the sequential method with standard error of 11%.

Greiby, et al. (2016) carried out estimation of kinetic parameters of anthrocyenin degradation in cherry Pomace using inverse method for non-isothermal heating.  $k$  and  $E_a$  -values at 115.8°C were respectively 0.0129 per min. and 75.7KJ/mol at 70% moisture content. This estimation was helpful in dynamic process design.

Mishra, et al [8] researched on the application of results for optimal experimental design of non linear models to enhance accuracy of parameters estimations.

Hofmanin, H. [9] researched on kinetic data analysis and parameter estimation which  $E_a$  and Arrhenius constant were determined and used for reactor model.

Dirion, et al [10] researched on Kinetic Parameter Estimation from Thermogravimetric Analysis (TGA). The two tools applied were the nonlinear parameter estimation procedure for identifying parameters in non linear dynamical models and computation of TGA required in order to identify the best kinetic parameters with high statistical reliability.

Sulaiman, [11] researched on Estimating the Kinetic Parameters of a starch viscosity model and with error of 12%. The  $K_g$  (rate constant) and activation Energy of gelatinization ( $E_g$ ) were estimated using non linear regression analysed.

Perry, et al, [12] worked on the estimation of kinetic parameters for both linear and non linear rate expressions such as Langmuir – Hinshelwood rate expression. Minimization of the sum of square of residuals does not result in a closed form for nonlinear parameter estimates as for linear case; rather it requires an iterative numerical solution, and having a reasonable initial estimate of the parameter values and feasible ranges are critical for success. The nonlinear regression procedure typically involves a steepest descent optimization search combined with Newton's linearization method when minimum is approached, enhancing the convergence speed [13-14].

Hirmajer, et al [15] developed a useful regression analysis on parameters estimation of activation energies. Broke, et al [16] brought to life a solver named non-linear programmer (NLP) which gave solutions on non-linear programming problems and be used to minimize the sum of squares of residuals errors.

Zamontrvy, P. & Belohlav, L. [17] produced a vital regression analysis software package (ERA). Its input data matrix was limited to 20 independent variables (20 responses) with almost 256 experimental points in a set of response and the models parameters to be estimated was limited to 15.

Appropriate steps was taken to achieved the research goal: to study the complex series-parallel reactions of the Naphtha lumps feed and hence develop the various rate expressions models for the Paraffins, Naphthenes, Aromatics & Gas (Naphtha lump feeds), to develop steady state models (mole fractions and temperature models) for the lumped kinetic scheme of industrial reformer using material and energy balance principles, subject the steady state results obtained from the simulation of the steady state models to optimization of activation energies, hence kinetic parameters of the various species of Naphtha lumps feed using regression analysis procedures, to obtain the optimal yields (i.e. mole fractions and temperature values of various species of Naphtha lumps feeds) from the optimal kinetic parameters

obtained from the optimization techniques, and to compare the optimal yields with steady states yields and literature data.

## 2. MATERIALS AND METHODS

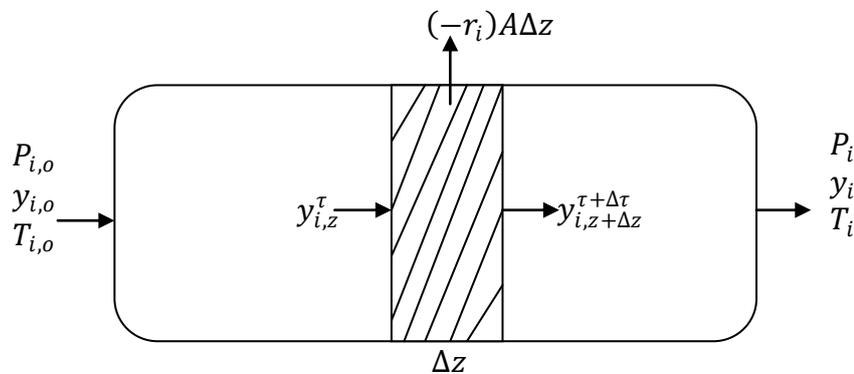
### Materials

Materials for the research are Naptha lump feeds, Optimization tool (single point Regression analysis tool and Marquardt-Levenberg algorithm), F-test table, and principle of conservation of mass and energy.

### Methods

The derivation of the reactor block model for this research maintains the following constraints (assumptions): There is continuous catalyst regeneration in the regenerator which keeps the catalyst at 100% efficiency; the reactor is stacked tabular plug flow reactor; models are derived from first principles of material and energy balance maintaining steady state process conditions; the reactor feed are low fractions Hydrocarbons ranging from C<sub>6</sub> – C<sub>8</sub>; models maintain a lumping scheme chemistry of the paraffins, Aromatics and Naphthenes; Hydrogen recycle shall equally maintained and the hydrogen seen in the reaction scheme is excess and serve as a catalyst for the reactions process, hence will not be used for the rate of reaction determination procedures.

### Fundamental Material Balance



**Fig. 1** Schematics Ideal flow with mole fraction, Partial Pressure and Concentration varying along the differential Length of the reactor

The steady state material models was derived from first principle using equation 1

$$\left\{ \begin{array}{l} \text{Rate of accumulation} \\ \text{of species, } i, \text{ in the} \\ \text{reactor} \end{array} \right\} = \left\{ \begin{array}{l} \text{Rate of inflow of} \\ \text{species, } i, \text{ into the} \\ \text{flow reactor} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of outflow} \\ \text{of species, } i, \text{ from} \\ \text{the flow reactor} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of depletion} \\ \text{of species, } i, \text{ due to} \\ \text{chemical reaction} \\ \text{within the flow reactor} \end{array} \right\} \quad (1)$$

$$u_f \frac{dy_i}{dz} + \frac{1}{c} (-r_i) = 0 \quad (2)$$

Where:

$u_f$  = superficial velocity entering the flow reactor; m/s

$v_o$  = Volumetric flow rate;  $m^3/s$

$A$  = Cross sectional area of the reactor;  $m^2$

$P$  = Total pressure of the system; atm

$R$  = Ideal gas constant; KJ/kmol.K

$T$  = Absolute Temperature; K

$C_{i,o}$  = Initial concentration of species; mol/L

$C_i$  = Final concentration of species; mol/L

$C$  = Total concentration, mol/L

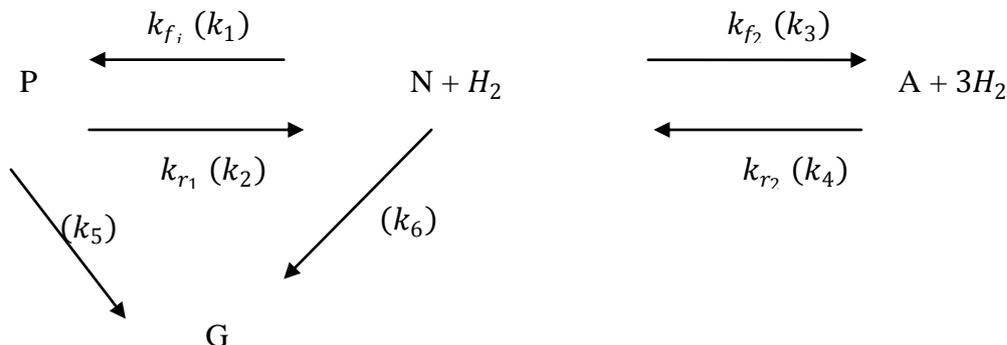
$P_i$  = Partial pressure of species, I; atm

$r_i$  = Rate of reaction of species, i; mol/s.L

$i$  = Naphthenes, Paraffins, Aromatics, Gases

**Kinetic Model Development**

Development of the kinetic lumps: (Naphtha, Paraffins, Aromatics and Gas). The reaction follows lumping scheme kinetics shown in Figure 2.



**Fig. 2** Composite five (5) –Lump Reforming Reactions [18]

The rate expressions for the composite five (5) lumps kinetics were stoichiometrically and by mass conservation principle developed to give the rates of the species of the naphtha lump feeds.

$$(-r_N) = \left(k_{f2} - \frac{k_{f2}}{k_{p2}} + k_6\right) P y_N - \left(\frac{k_{f1}}{k_{p1}} + k_{f1}\right) P y_P \tag{3}$$

$$(-r_A) = \frac{dy_A}{dt} = -k_{f2} P y_N + k_{r2} P y_N = \left(\frac{k_{f2}}{k_{p2}} - k_{f2}\right) P y_N \tag{4}$$

$$(-r_P) = \left(\frac{k_{f1}}{k_{p1}} - k_{f1} + k_5\right) P y_P \tag{5}$$

$$(-r_G) = \frac{dy_G}{dt} = -k_5 P y_P - k_6 P y_N \tag{6}$$

Where:

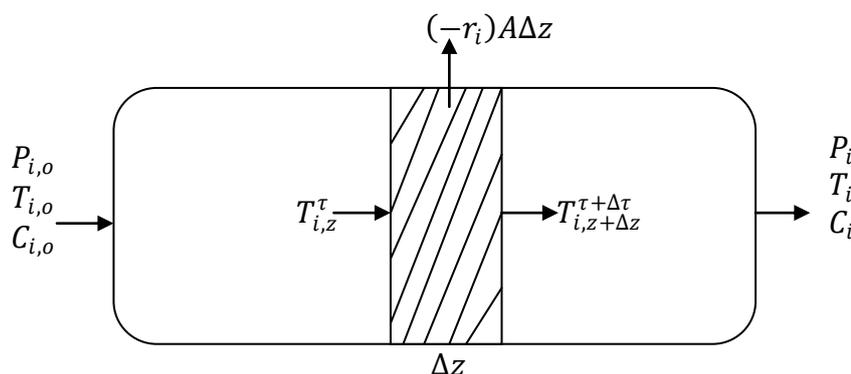
$y_N$  = mole fraction of Naphthenes, mol

$y_A$  = mole fraction of Aromatics; mol

$y_P$  = mole fraction of paraffins, mol

$r_i$  = rate of reaction for species,  $i = (N, A, P, \& G)$ ; mol/s

**Energy Balance (Temperature Model Development)**



**Fig. 3** Sketch of a cross-section of PFR showing temperature variation along the flow reactor (in the z-direction) The Energy balance equation is stated as thus:

$$\left\{ \begin{array}{l} \text{Rate of Accumulation} \\ \text{of energy within the} \\ \text{differential element of} \\ \text{the reactor of species} \end{array} \right\} = - \left\{ \begin{array}{l} \text{Rate of outflow of} \\ \text{energy of species } i, \\ \text{from the differential} \\ \text{element of the reactor} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of inflow of} \\ \text{energy into the} \\ \text{differential element} \\ \text{of the reactor of species, } i \end{array} \right\} + \left\{ \begin{array}{l} \text{Rate of depletion of} \\ \text{energy of species, } i, \text{ within} \\ \text{the differential element} \\ \text{of the reactor due to Bio} \\ \text{chemical reaction processes} \end{array} \right\} + \left\{ \begin{array}{l} \text{Rate of energy added} \\ \text{into the differential} \\ \text{element of the reactor} \end{array} \right\} \quad (7)$$

Mathematical Analysis of equation (7) at steady-state gives the temperature model

$$\frac{dT}{dz} + \frac{1}{u_f \rho C_p} \left( (-r_N)(\Delta H_N) + (-r_A)(\Delta H_A) + (-r_P)(\Delta H_P) + (-r_G)(\Delta H_G) \right) = 0 \quad (8)$$

Where:

$\rho$  = density, Kg/m<sup>3</sup>

$C_p$  = Specific heat capacity KJ/Kg.K

$(\Delta H_{r_i})$  = Heat of reaction of species,  $i$ , KJ/Kmol

$i = (N, A, P \text{ and } G)$

$u_f$  = Superficial velocity, m/s

### Parameter Estimation

#### Optimization Procedures for Estimation of kinetic parameters of Naphtha lump feeds (P, N, A, & G)

The single point regression analysis search is applied for the estimation of activation energies and pre-exponential factor of the various species (P, N, A, & G) of the Naphtha lump feeds. Below steps are necessary for the optimization procedures.

Step 1: Steady state mole fractions and temperature models derived above are solved numerically using Runge-Kutta algorithm (ode 45 MATLAB Solver).

Step 2: Steady state yields of mole fractions and temperature obtained from the Simulation process are compared with the plant data to get percentage deviations of the Naphtha lump feeds (Paraffins, Naphthenes, Aromatics and Gas).

Step 3: Steady state yields of the mole fractions and temperature of the species are then subjected to Optimization procedures:

The objective function (S) for the optimization method is given:

$$S = \sum_{i=1}^4 \left\{ (y_{i,plant} - y_{i,cal})^2 + (T_{0,plant} - T_{0,cal})^2 \right\} \quad (9)$$

Subject to (Constrain functions) given as:

$y_{P,0} = 0.3478 \text{ mol}; y_{N,0} = 0.5144 \text{ mol}; y_{A,0} = 0.1378 \text{ mol}; y_{G,0} = 0 \text{ mol}; T_0 = 780K$

$y_{i,0} \geq 0; T_0 \geq 0, i = P, N, A \text{ \& } G$

$y_{i,cal}$  &  $T_{cal}$  = Computed from ode 45-solver

The statistical test approach i.e.  $F_{cal}$  as the convergence or boundary limit for the iteration optimization process is stepwise stated below:

➤  $y_{i,plant}$  &  $T_{plant}$  = obtained from literature (plant data) or initial boundary conditions

➤  $\bar{y}_i$  = mean value of  $y_i$  i.e.  $\bar{y}_i = \frac{\sum y_i}{n}; n = 41$

➤  $\bar{T}$  = mean value of T, i.e.  $\bar{T} = \frac{\sum T}{n}; i = P, N, A \text{ \& } G$

➤ Compute the Sum of Residual Errors (SSE)

$$SSE = \sum_{i=1}^4 \left\{ (y_{i,plant} - y_{i,cal})^2 + (T_{0,plant} - T_{0,cal})^2 \right\}$$

➤ Compute the Sum of Square Mean (SSM)

$$SSM = \sum_{i=1}^4 \left\{ (y_{i,cal} - \bar{y}_{0,cal})^2 + (T_{0,cal} - \bar{T}_{0,cal})^2 \right\} \quad (10)$$

➤ Compute  $F_{cal}$

$$F_{cal} = \frac{\frac{SSM}{p}}{\frac{SSE}{n-p}} = \frac{MSM}{MSE} \quad (11)$$

Where:

Mean of Square Mean (MSM) =  $\frac{SSM}{p}$

Mean of Square Error (MSE) =  $\frac{SSE}{n-p}$

Where:

$p$  = number of kinetic parameters to be optimized and

$n$  = number of points or experimental results obtained from the simulations

➤ Compute  $F_{tab}$  from 5% confidence level

$$1-\alpha = 1 - 0.05 = 0.95$$

Degree of freedom of Error (DFE) =  $n - p$

- Compute for the corrected degree of freedom (DFM)

$$\text{DFM} = p - 1$$

$qf = (1-\alpha, p - 1, n - p)$  i.e.  $qf(0.95, 3, 37)$  for  $n = 41, p = 4$

$F_{\text{tab}}$  is gotten from table of F – test on range (3, 37) at 95% confidence level.

- Choose  $\alpha$  such that  $0 < \alpha < 1$

$$\alpha = 0.85$$

- Computer for new Activation Energies

$$E_i^{j+1} = E_i^j + \alpha \Delta \quad (12)$$

Where:

$$\Delta (\text{increment}) = -(J_r J_r^T)^{-1} J_r$$

$J_r = \text{matrix of } (n \times p)$

$J_r^T = \text{transpose of } J_r \text{ matrix, i.e. } (p \times n)$

Thus;

$$\Delta = -[(n \times p)(p \times n)]^{-1}(n \times p) \quad (13)$$

- From the table of F-test,  $F_{\text{tab}}$  is gotten as:

At 95% confidence level (C.L)

$$F_{\text{tab}} = 2.911$$

- From the  $F_{\text{tab}}$  at 95% C.L

$$F_{\text{tab}} = 2.278$$

- Termination Criterion

If  $F_{\text{Cal}} \geq F_{\text{tab}}$ , stop iteration and the  $E_i$ -values are obtained, else continues till  $F_{\text{Cal}} \geq F_{\text{tab}}$

- The optimal values of  $E_i$  to obtained the optimal kinetic parameters i.e. rate constants,  $k_i$

$$k_i = k_{i,0} \exp\left(\frac{-E_i}{RT}\right) \quad (14)$$

$i = P, N, A \& G$

Step 4: The optimal  $k_i$ -values obtained from equation (14) is used to get optimal yields of the mole fractions and temperature of the various species.

### Operating Parameters

Table -1 Literature data  $A_o, k_p, k_f, k_r$  &  $\Delta H_R$  [3]

Reactor 3	$A_o$	Rate constant	$\Delta H_R \frac{KJ}{Kmol}$ of $H_2$ lib
Conversion of naphthenes to aromatics	$1.19 \times 10^8$	$1.040 \times 10^6 \exp\left[46.15 - \frac{212700}{RT}\right]$	70928
Conversion of paraffins to naphthenes	$4.170 \times 10^{13}$	$9.869 \times 10^3 \exp\left[\frac{36950}{RT} - 712\right]$	-44185
Naphthenes cracking	4.5881E18	—	-51860
Paraffin cracking	4.5881E18	—	-51860

Table -2 Summary of literature data [3]

Reactor	Parameters	
	Activation Energies $E_i$ , KJ/Kmol	Rate constant ( $k_i$ )
Conversion of Paraffins to Naphthenes	$E_P (E_1) = 356460$	$4.17E12 * \exp\left[\frac{-E_1}{RT}\right]$
Conversion of Naphthenes to Aromatics	$E_N (E_2) = 174500$	$1.19E08 * \exp\left[\frac{-E_2}{RT}\right]$
Naphthenes hydrocracking	$E_A (E_3) = 394380$	$4.5881E18 * \exp\left[\frac{-E_3}{RT}\right]$
Paraffins hydrocracking	$E_G (E_4) = 394380$	$4.5881E18 * \exp\left[\frac{-E_4}{RT}\right]$

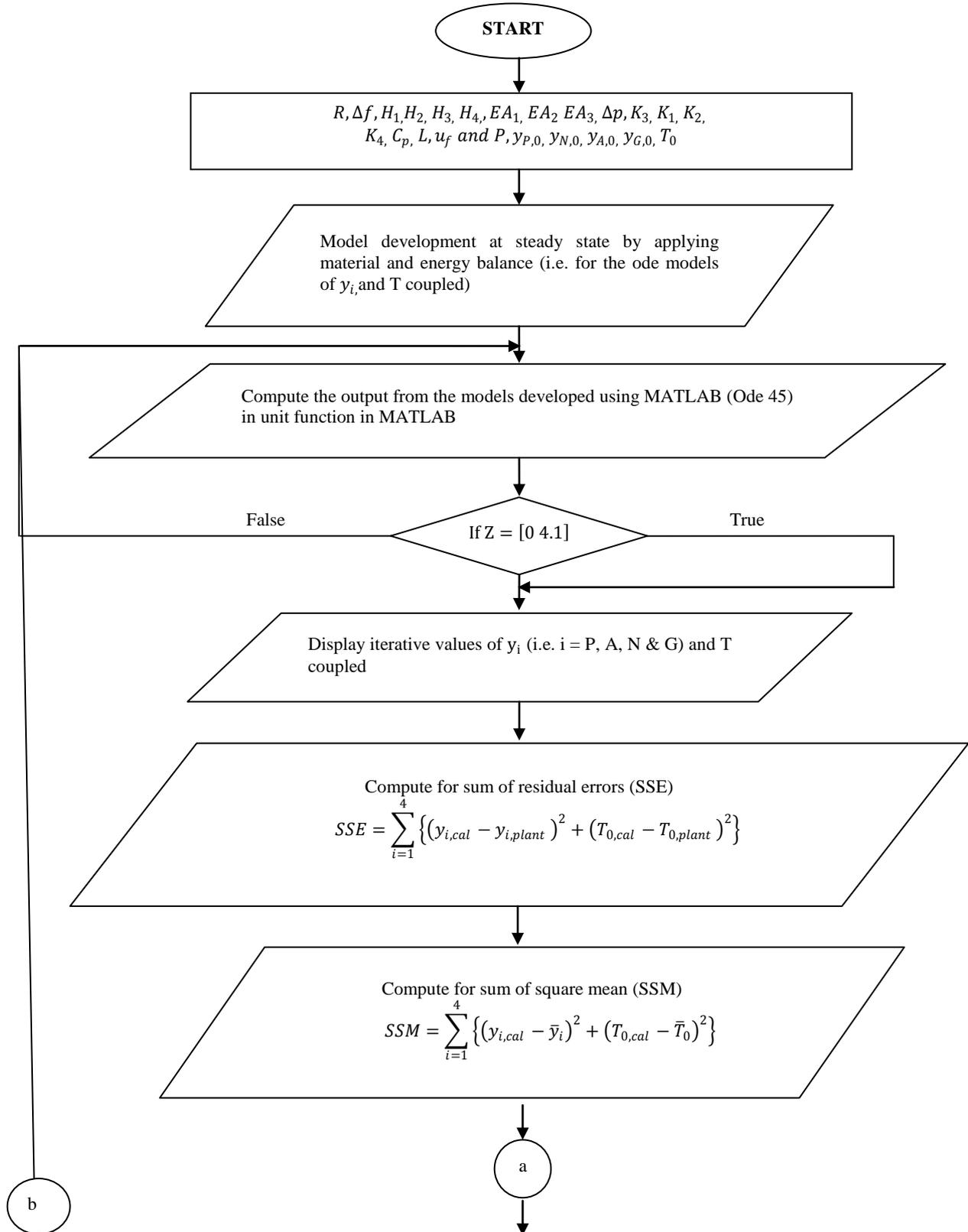
Other operating parameters for the programming and the optimization process are stated:

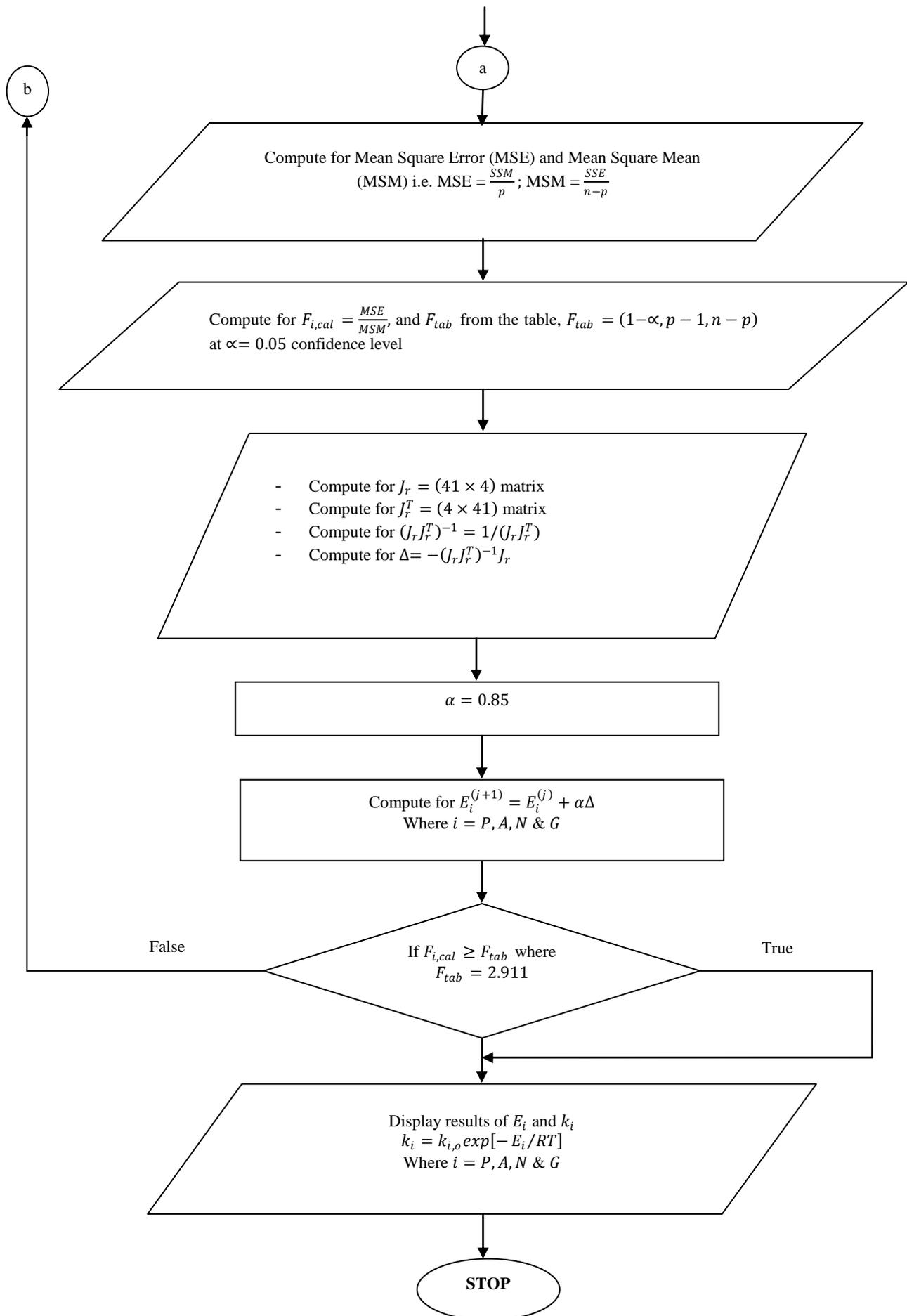
$$y_{P,0} = 0.3478 \text{ mol}; y_{N,0} = 0.5144 \text{ mol}; y_{A,0} = 0.1378 \text{ mol}; y_{G,0} = 0 \text{ mol}; T_0 = 780K$$

P=709.275KPa and see also Appendix II for additional operating parameters applied for the resolutions of the models and optimization process.

**Flow Chart for the Optimization Computation to Estimate Activation Energies**

**FLOWCHART**





### 3. RESULTS AND DISCUSSION

The results presented below show the estimation of kinetic parameters of the naphtha lump feeds (Paraffins, Naphthenes, Aromatics and Gas). The results follow optimization algorithm and flow chart presented. MATLAB compiler was used to simulate the models to give steady states and optimal yields of the mole fractions of the Hydrocarbons (HCs) lumps (i.e. naphtha lump feeds). Then steady state results obtained were subjected to optimization process to estimate the kinetic parameters (activation energies and pre-exponential factors). Various results are displayed below in tables and figures which were equally discussed.

**Table -3 Results of Optimal Kinetic Parameters of HCs Lumps**

PARAMETERS	$E_i$ (KJ/Kmol)	$A_i$
Paraffins	354950	3.5445E12
Naphthenes	173566	1.30E08
Aromatics	395001	3.212E18
Gas	394005	5.414E18

Table 3 shows results of activation energies and pre-exponential factors obtained from the optimization process. The values for the various species have considerable changes from the plant values.

**Table -4 Results Optimal Yield of Naphtha Lump Feeds**

Z	$y_P$	$y_N$	$y_A$	$y_G$	T
0	0.3478	0.5144	0.1378	0	780
0.5	0.3476	0.509	0.233	1.16E-05	780.02
1.0	0.347	0.461	0.344	2.52E-05	780.04
1.5	0.336	0.433	0.406	3.88E-05	780.06
2.0	0.33	0.344	0.568	5.25E-05	780.08
2.5	0.30	0.256	0.68	6.61E-05	780.10
3.0	0.26	0.217	0.791	7.97E-05	780.12
3.5	0.22	0.130	0.903	9.34E-05	780.14
4.0	0.20	0.094	1.00	1.07E-04	780.16
4.1	0.20	0.094	1.00	1.07E-04	780.16

Table 4 depicts the results of optimal yields of the various species obtained due to the estimated  $E_i$  &  $A_i$  values from the optimization process carried out.

**Table -5 Results for SSP Yield of Various Species of Naphtha Lump Feeds**

Z	$y_P$	$y_N$	$y_A$	$y_G$	T
0	0.3478	0.5144	0.1378	0	780
0.5	0.347	0.501	0.233	1.16E-05	780.0163
1.0	0.3462	0.462	0.345	2.53E-05	780.0367
1.5	0.3401	0.323	0.457	3.90E-05	780.057
2.0	0.3000	0.282	0.569	5.26E-05	780.0774
2.5	0.2650	0.240	0.681	6.63E-05	780.0978
3.0	0.2020	0.201	0.793	8.00E-05	780.1181
3.5	0.1980	0.193	0.905	9.37E-05	780.1385
4.0	0.1500	0.145	1.000	1.08E-04	780.1589
4.1	0.1050	0.104	1.000	1.09E-04	780.1629

Where: SSP = Steady-state process

Table 5 show steady state yields of mole fractions and Temperature of the various species of the naphtha lumps feed obtained from numerical integration using 4<sup>th</sup> order Runge-Kutta algorithm as a result of models developed.

**Table -6 Comparison of optimum activation energies with plant  $E_i$**

Parameters	Optimum $E_i$	Plant $E_i$	Deviation (%)
Lumps (reformat)	$E_i$ (KJ/Kmol)	$E_i$ (KJ/Kmol)	D
Paraffins	354950	356460	0.424
Naphthenes	173566	174500	0.535
Aromatics	395001	394380	0.0157
Gas	394005	394380	0.0951

Table 6 show the comparison of the estimated activation energies of various species of naphtha lumps feed with plant value obtained from Wordu, [3]. The deviations are reasonable and thus indicate that the optimization approach is good.

**Table -7 Comparison of estimated Arrhenius constant with literatures of Naphtha Lumps feed**

Parameters	Pre-exponential factor $A_{i,0}$	Arrhenius constant $A_i$	Deviation (%)
Paraffins	4.17E12	3.5445E12	15
Naphthenes	1.19E08	1.30E08	9
Aromatics	4.5881E18	3.212E18	30
Gas	4.5881E18	5.414E18	18

Table 7 depicts the percentage deviation of the pre-exponential factors (Arrhenius constants) with plant or literature values. The deviations of the various species of naphtha lumps feed (P, N, A, & G) are reasonable and explained that the approach utilize for the optimization process is a better one.

**Table -8 Results of rate constants calculated from optimal  $E_i$ ,  $A_i$ , &  $T_{o,cal}$  values obtained above**

Parameters	$k_i$	$k_i$
Paraffins	$3.545E12 * \exp\left(\frac{-354950}{RT}\right)$	5.63E-12
Naphthenes	$1.30E08 * \exp\left(\frac{-173566}{RT}\right)$	2.46E-04
Aromatics	$3.212E18 * \exp\left(\frac{-395001}{RT}\right)$	1.79E-08
Gas	$5.414E18 * \exp\left(\frac{-394000}{RT}\right)$	1.56E-08

Table 8 shows the calculated rate constants from the estimated activation energies, Arrhenius constants and optimal Temperature values obtained from the optimization process. The results gave a good estimate of the parameters and should be followed and adopted.

**Table -9 Comparison of optimum kinetic parameters with literature  $k_i$  from table 2**

Parameters	Optimum $k_i$	literature $k_i$	Deviation (%)
Lumps (reformate)	$k_i$	$k_i$	D
Paraffins	5.63E-12	5.5981E-12	0.570
Naphthenes	2.46E-04	2.451E-04	0.367
Aromatics	1.79E-08	1.77845 E-08	0.650
Gas	1.56E-08	1.77845 E-08	12

Table 9 shows the deviation of rate constants of the various species of the naphtha lumps feed gotten as a result of plant data and the estimated activation energies, Arrhenius constants and Temperature respectively.

**Table -10 Comparison of optimum Yield with SSV**

Parameters	Optimum yield	SSV	Deviation
Lumps (reformate)	Mole	Mole	D
Paraffins	0.25406	0.26011	0.023
Naphthenes	0.30524	0.29654	0.029
Aromatics	0.60628	0.61208	0.0095
Gas	5.8146E-05	5.8544E-05	0.0068
Temperature	780.088	780.0815	0.0000385

Where: SSV= Steady-State Values; OY = Optimum Yield

Table 10 indicates comparison of the optimal yield with steady state yield. The deviations shows that there is a difference in the two results as optimization procedures gave a better estimates of kinetic parameters to the literature ones, hence variation of the yields.

**Table -11 Comparison of Optimum Yield with Literature Data**

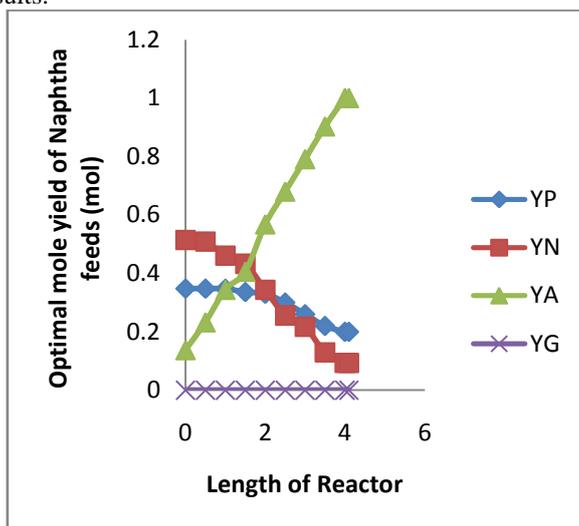
Parameters	Model Predictions	Lit. Data	Deviation
Lumps (reformate)	Mole	Mole	D
Paraffins	0.25406	0.3478	0.26
Naphthenes	0.30524	0.5144	0.41
Aromatics	0.60628	0.1378	3.4
Gas	5.8146E-05	0	-
Temperature	780.088	780	0.00011

Table 11 indicates comparison of the optimal yield with the literature data. The deviation shows that the estimated kinetic parameters differ from the literature ones. Hence optimization process gave better yields (optimal yields).

**Table -12 Comparison of Steady State Values with Literature Data**

Parameters	Literature data	SS-values	Deviation
Lumps (reformat)	Mole	Mole	D
Paraffins	0.3478	0.26011	0.25
Naphthenes	0.5144	0.29654	0.42
Aromatics	0.1378	0.61208	3.44
Gas	0	5.854E-05	-
Temperature	780	780.0815	0.0001

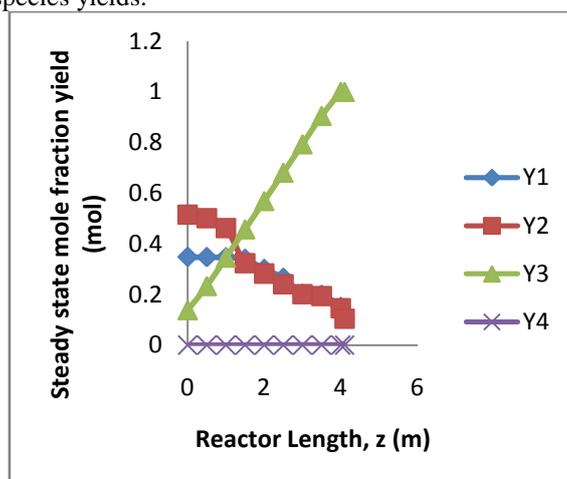
Table 12 depicts comparison of the steady state yield and plant data. The deviation indicates the essence of this research for the estimation of kinetic parameters, but the deviation are below and small indicating the accuracy of the method applied in the research to give results.



**Fig. 3** Optimal mole fractions yields varying with reactor length

Figure 3 depicts optimal yield of mole fractions for the various species (P, N, A, & G) of the Naphtha lumps feed with the reactor length. The result shows that there is progressive increase in the mole fractions of Aromatics and Gas respectively starting from YA=0.1378mole and YG=0mol at z=0m to respectively YA=1mol and YG=0.000107mol at z=4m.

The optimal yield of paraffins and Naphthenes decreases from YP=0.3478mol and YN=0.5144mol to YP=0.20mol and YN=0.094mol at z=0m to z=4m respectively. This is due to the kinetic scheme of the complex series-parallel reactions in the reformer cracks to give more than one products and heat involved in the process. The optimal yields are gotten as a result of the estimated kinetic parameters (activation energies and pre-exponential factors) using single point regression analysis iterative optimization process. These optimal kinetic parameters were subjected back to the algorithm of optimization to generate various species yields.



**Fig. 4** Steady state yield mole fractions of naphtha lump feeds varying with reactor length

Figure 4 shows the steady state yields of mole fractions of the various species (P, N, A, and G) of the Naphtha lump feeds varying along the reactor length. The graph shows that the yield of paraffins and naphthenes decreases from Y1=0.3478mol and Y2=0.5144mol at z=0m to Y1=0.1050mol and Y2=0.104mol respectively at z=4m. Aromatics and

gas are also produced from the reaction process. The yield of Gas and Aromatics increases from  $Y_4=0\text{mol}$  and  $Y_3=0.1378\text{mol}$  at  $z=0\text{m}$  to respectively  $Y_4=0.000109\text{mol}$  and  $Y_3=1.0\text{mol}$  at  $z=4\text{m}$ .

Decrease in yield of paraffins and naphthenes indicate they depletes to gives Aromatics, and Gas ( $C_1 - C_4$  fractions) and at a long run, the decreases becomes constant in the reactor. The steady state models gave the various yields in mol and results proved that the models were better developed.

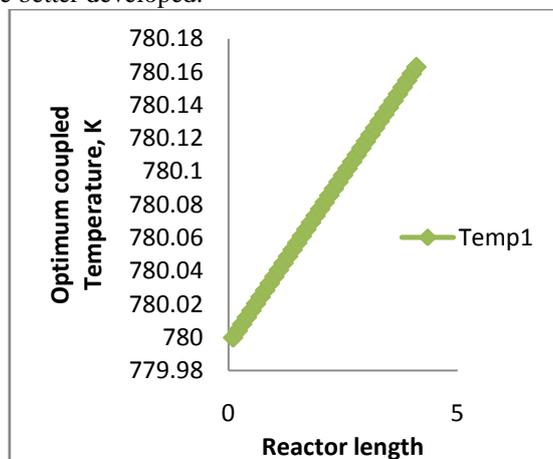


Fig. 5 Optimum Temperature against Reactor length

Figure 5 shows endothermic process occurring in the reformer and heat increases along the reformer but in small quantity as shown above. The profile indicates that at optimal functioning of the reactor, very small amount of heat is added as 780K to 780.18K is the range of heat in the reformer.

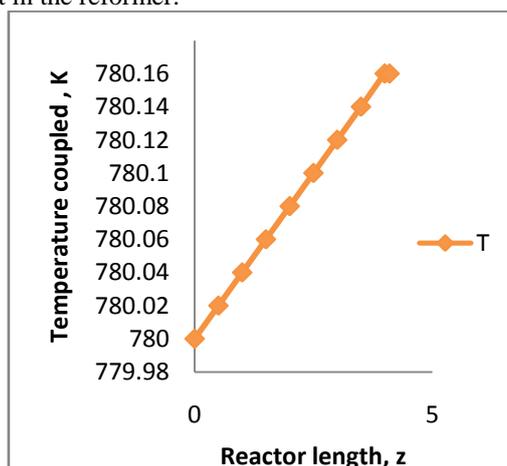


Fig. 6 Steady state variation of Temperature with Reactor length

Figure 6 indicates steady state temperature profile varying along the reactor. The reaction process occurring in the reformer is endothermic process showing that heat is added but in small quantity as indicated in the plot. The temperature in Kelvin increases as reactor length increases from  $z=0\text{m}$ ,  $T=780\text{K}$  to  $z=4\text{m}$  when  $T=780.1625\text{K}$ .

#### 4. CONCLUSION

The development of steady-state model for component species of P, N, A, and G and temperature of Naphtha reactor was achieved applying principles of conservation of mass and energy. The Kinetic Expressions were developed from the series-parallel reactions taking place in the reactors.

The ordinary differential equations developed were solved and simulated using mat-lab Ode-45-solver. Various results are tabulated in Tables 3 to 12 and profile plots are shown in figures 3 to 6

The steady state models prediction results were subjected to optimization process (i.e. single point regression analysis) to estimate the activation energies and pre-exponential factor of the paraffins, naphthenes, aromatics and gas. The optimal yields were obtained from the updated parameters.

#### Nomenclature

##### Symbol Definition

$E_a$	Activation Energy
$\Delta H$	Enthalpy Change
$T$	Absolute Temperature
$R$	Gas constant

##### Unit

$KJ/Kmol$
$KJ/Kmol$
$K$
$KJ/Kmol K$

$A$	Pre-exponential factor/frequency factor or Arrhenius constant	
$\rho_i$	Density of species $i$	$Kg/m^3$
$\rho_\tau$	Total Density	$Kg/m^3$
$y_i$	Mole fraction of species	$i, mol$
$SS$	Sum of squares	-
$\Delta$	Incremental value	-
$r_i$	Rate of reaction of species,	$i, mol/m^3s$
$PESS$	Pure error sum of squares	-
$RSS$	Regression sum of square	-
$v_o$	Volumetric flow, $m^3/s$	
$\Delta H_{r,i}$	Change of Heat of Reaction of species,	$i = N, P, A\&G KJ/Kmol$
$Q$	Quantity of heat,	$KJ/s (KW)$
$q$	heat per unit volume	$KW/m^3$
$C_p$	Specific heat capacity	$KJ/Kmol K$
$u_f$	Superficial velocity,	$m/s$
$k_p$	Equilibrium constant	$KJ/Kmol$
$k_f$	Rate constant of forward reaction	
$k_r$	Rate constant of reverse reaction	

### REFERENCES

- [1]. Wenyu, S. & Ya-Xiang, Y. (2010) *Optimization Theory and Methods: Nonlinear Programming*, China: Springer, 541.
- [2]. Dechter, R. (2003). Constraint Processing, *Artificial Intelligent Journal*, USA: Morgan Kaufmann: 780-782.
- [3]. Wordu, A. A. (2009). Dynamic simulation of industrial reformer reactor (DSIRR) Ph.D. dissertation Rivers State University of Science and Technology, Port Harcourt, Nigeria.
- [4]. Erik, R., & Gustavo, M. (2006) Estimation of Activation Energies during hydro-desulfurization of middle distillates *Journal of Science Direct copyright (c) 2017 Elsevier B.V*
- [5]. Dolan, K. D., Yang, L. & Trampel, C. P. (2006). Nonlinear regression technique to estimate kinetic parameters and confidence intervals in unsteady state conduction-heated foods, *Journal of Food Engineering* 80(2): 581-593.
- [6]. Periago, P. M., Leontidis, S., Fernandez, P.S., Rodrigo, C & Martinez, A. (1998). Kinetic parameters of *Bacillus stearothermophilus* spores under isothermal and non-isothermal conditions, *Journal of Food Science and Technological International* 4(6): 443-447.
- [7]. Mishra, D., Dolan, K. D. & Yand, L. (2011). Bootstrap confidence intervals for kinetic parameters of degradation of anthocyanin in grape Pomace, *Journal of Food Processing Engineering*, 34(4): 1220-1233.
- [8]. Mishra, D; Dolan, K.D & Beck J.V (2009). Optimal Experimental Design to Estimate Thermal Degradation Kinetic Parameters for Nutraceuticals in Inter-mediate moisture foods: *American Society of Agricultural and Biological Engineers*, Michigan, www.asabe.org.
- [9]. Hofmann, H. (2003). Kinetic Data Analysis and Parameter Estimation. *Chemical Reactor Design and Technology*, 110: 69-105.
- [10]. Dirion, I. L. & Cabassud, M. (2008) Kinetic Parameter Estimation from TGA: Optimal design of TGA experiments, *Chemical Engineering Research and Design*, 36(6): 618-625.
- [11]. Sulaiman, R. (2011). Estimation of Kinetic Parameter in a Corn Starch viscosity model at different amylase contents, PhD Dissertation, Food Science Department, Biosystem Engineering, Michigan State University.
- [12]. Perry GH, Dominy NJ, Claw KG, Lee AS, Fiegler H, Redon R (2007). Diet and evolution of human amylase gene copy number variation. *Nature Genet.*, 39: 1256–1260.
- [13]. Marquardt, D. W. (1963). Algorithm for the least-squares estimation of non-linear parameters: *SIAM Journal on Applied Mathematics*, 11(2), 431-441.
- [14]. Levenberg, K. (1944). A method for the solution of certain non-linear problems in least squares: *Quarterly of Applied mathematics*, 2(2), 164-168.
- [15]. Hirmajer, T., Balsa-Canto, E., & Banga, J. R. (2009). DOTcvpSB, a software toolbox for dynamic optimization in systems biology. *BMC bioinformatics*, 10(1), 199.
- [16]. Brooke, P. P., Russell, D. W., & Price, J. L. (1988). Discriminant validation of measures of job satisfaction, job involvement, and organizational commitment. *Journal of applied psychology*, 73(2), 139.
- [17]. Zamontvry, P. & Belohlav, L. (1999) A Software for Regression Analysis of Kinetic data, *Journal of Computers & Chemistry*, 23: 479.
- [18]. Wordu, A. A. (2003). Modeling and simulation of petroleum naphtha reforming, M. Tech Thesis Rivers State University, Port Harcourt, Nigeria.