

## ACTIVATION ENERGIES PARAMETERS STATISTICAL SEARCH ESTIMATES FOR OPTIMALITY

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### ABSTRACT

The paper is a corollary consistency research of constrain statistical search technique to estimate activation energies of hydrocarbon lumps of crude oils. The typical lumps of hydrocarbons species in petroleum are the paraffin olefins naphthene and aromatics PONA. The crude oil lumps in this work are Paraffin naphthene, aromatics PNA plus gases. A mathematical optimal search for the best convergence of F-Test set at 2.911 values greater than or equals to F-calculated values were carried out for a maximum of 41-iterations on each species totaling 164 search for the activation energy  $E_i$  of Paraffin aromatics naphthene and gas. The results of the search process are given as: 356451.71KJ/Kmol; 174494.90KJ/Kmol; 394295KJ/Kmol and 394385KJ/Kmol of P, N, A and G species respectively. The optimal  $E_i$ -values gave updated  $k_i$ -values of 5.63E-12; 2.46E-04; 1.76E-08 and 1.78E-08 of P, N, A and G. Deviations from literature values shows 0.425%, 0.535%, 0.0157% and 0.0951% and 0.57%, 0.361%, 0.65% and 12% for  $E_i$ -values and  $k_i$ -values of P, N, A, & G respectively. These values can confidently be applied to reactor design and model simulation studies.

**Keywords:** Statistical search, activation energies, HCs-lumps, model, convergence.

### INTRODUCTION

Procedurally, it is essential when crude oil is stricken during prospecting, exploration and exploitation stage to carry out assaying to ascertain the extent of the paraffin, olefin, naphthene, and aromatics (PONA analysis), specific gravity and associated compounds (e.g. sulphur, heavy metals) and water content by the IOC majors.

The action is to determine the primary quality of the crude oil. However, much more than that is the kinetic parameters of each lump for reaction process in reactor design and modeling. Hence, these parameters control chemical reactions engineering processes i.e chemical reactor design.

Therefore, the present research is a corollary for consistency on the literature model equations [9] and [10] concepts of evaluating kinetic parameters of species in a lumped manner for chemical reactions processes. Equation [1] is a transcendental model equation and difficult to solve analytically for the activation energies  $E_i$  and rate constants  $K_{i,j}$ . Estimate of the activation energies,  $E_i$  for each of the kinetic lumps with the pre-exponential factor  $A_{oi,j}$  is achieved. The equilibrium constant  $K_p$ , parameter in the reversible reactions can be calculated from thermodynamic considerations. There are no significant differences between the values reported in literature of [Smith, 1959]; [Senifeld & Lapidus, 1974]; [Bommannan, Srivastava, & Saraf, 1989]; [Radosz & Kramarz, 1978]; [Van der Baan, 1980]; [Oboho, 2005]; and [Wordu, 2009] doctoral thesis dynamic simulation of reformer reactor.

And, most recently [Ojong & Wordu, 2018]; and [Wordu, 2018] posited strong hold of present research as the statistical constrain techniques of obtaining activation energies of the feeds rather than the prevalent calculus integration search for maximum and minimum values to obtain optimum convergence values for earlier literatures estimations. Because, the activation energies depend on catalyst composition in the absence of reliable experimental values can best be estimated from plant data obtained from refinery reactor plant Alesa Eleme, Port Harcourt-Nigeria.

Constrain statistical search for optimum was applied to estimate the activation energies that minimized the sum of the squares of the differences between calculated and experimental values of dimensionless reactor outlet temperatures and mole fractions of the various lumps from the third reactor simultaneously. Plant data for the mole fractions at the outlet of the first two reactors were not available because the reactors 1 and 2 are in continuous catalyst cracking process and could not be used in the parameter estimation because reactor 3 is the end [outlet] of reaction process.

The dimensionless reactor temperature was defined as the ratio of the outlet temperature to the inlet temperature.

## MATERIALS AND METHOD

### MATERIALS

The research is purely a mathematical search for optimum convergence point for lumped feed reactions kinetic parameters. Hence, it is analytically statistical search technique. The prerequisite materials are the literature plant data, kinetic-model-lumps, constrain optimization model, and software. The reactor feed of the hydrocarbon lumps of paraffin, naphthene, aromatics, and reactor temperature.

### METHOD

#### CONSTRAIN STATISTICAL SEARCH MODE

The material and temperature rate model stated mathematically for brevity as coupled compact model that explains the process is expressed as:

$$\text{Rate} = A_0 \exp -E_1/RT [P_A; P_N; P_P; P_G; T_R] \quad [1]$$

Equation [1] can be replicated *w.r.t* mole and/or mass fraction of the feed material in the reactors.

$$(-r_N) = -k_{r_1} P_P + k_{f_1} P_N P_{H_2} + k_{f_2} P_N P_{H_2} - k_{r_2} P_A P_{H_2}^3 + k_6 P_N P_{H_2} \quad [2]$$

Expressing equation [2] in terms of mole fractions ( $y_i$ ) and

Equation [2] becomes:

$$\begin{aligned} (-r_N) &= -C_T \frac{dy_N}{d\tau} = k_{f_1} P_T^2 y_N y_{H_2} + k_{f_2} P_T^2 y_N y_{H_2} + k_6 P_T^2 y_N y_{H_2} \\ &\quad - k_{r_1} P_T y_P - k_{r_2} P_T^4 y_A y_{H_2}^3 \\ (-r_N) &= (k_{f_1} + k_{f_2} + k_6) P_T^2 y_N y_{H_2} - \frac{k_{f_1}}{k_{P_1}} P_T y_P - \frac{k_{f_2}}{k_{P_2}} P_T^4 y_A \end{aligned} \quad [3]$$

$$\begin{aligned} (r_A) &= C_T \frac{dy_A}{d\tau} = k_{f_2} P_T^2 y_N y_{H_2} - k_{r_2} P_T^4 y_A y_{H_2}^3 \\ &= k_{f_2} P_T^2 y_N y_{H_2} - \frac{k_{f_2}}{k_{P_2}} P_T^4 y_A y_{H_2}^3 \end{aligned} \quad [4]$$

$$\begin{aligned} (-r_P) &= -C_T \frac{dy_P}{d\tau} = k_{r_1} P_T y_P - k_{f_1} P_T^2 y_N y_{H_2} + k_5 P_T y_P \\ &= \frac{k_{f_1}}{k_{P_1}} P_T y_P - k_{f_1} P_T^2 y_N y_{H_2} + k_5 P_T y_P \end{aligned}$$

$$= \left( \frac{k_{f1}}{k_{P1}} + k_5 \right) P_T y_P - k_{f1} P_T^2 y_N y_{H_2} \quad [5]$$

$$\begin{aligned} (r_{H_2}) &= \frac{dy_{H_2}}{d\tau} = k_{r1} P_T y_P - k_{f1} P_T^2 y_N y_{H_2} - k_6 P_T^2 y_N y_{H_2} \\ &(-k_{f2} + k_{r2}) P_T^2 y_N y_{H_2} + (k_{f2} - k_{r2}) P_T^4 y_A y_{H_2}^3 \\ &= \frac{k_{f1}}{k_{P1}} P_T y_P - K_{f1} P_T^2 y_N y_{H_2} - K_6 P_T^2 y_N y_{H_2} - K_{f2} P_T^2 y_N y_{H_2} + \frac{k_{f2}}{k_{P2}} P_T^2 y_N y_{H_2} \\ &+ k_{f2} P_T^2 y_A y_{H_2}^3 - \frac{k_{f2}}{k_{P2}} P_T^4 y_A y_{H_2}^3 \\ (r_{H_2}) &= \frac{k_{f1}}{k_{P1}} P_T y_P + \left( \frac{k_{f2}}{k_{P2}} - k_{f1} - k_6 - k_{f2} \right) P_T^2 y_N y_{H_2} + \left( k_{f2} - \frac{k_{f2}}{k_{P2}} \right) P_T^4 y_A y_{H_2}^3 \end{aligned} \quad [6]$$

$$(r_G) = C_T \frac{dy_G}{d\tau} = k_5 P_T y_P + k_6 P_T^2 y_N y_{H_2} - k_7 P_T y_G \quad [7]$$

## OBJECTIVE FUNCTION

The objective function is defined mathematically as:

$$S = \sum_1^m \left[ \sum_{i=1}^3 (N_{i \text{ calculated}} - N_{i \text{ plant}})^2 + \sum_{j=1}^3 (T_{out \text{ calculated}} - T_{out \text{ plant}})^2 \right] \quad [9]$$

Where,

$m$  = number of data sets used

$i = 1, 2$  and  $3$  for naphthene, paraffin and aromatic hydrocarbon

$j = 1, 2$  and  $3$  for reactor 1, 2 and 3 respectively.

For assumed value of  $E_i$ , equations 1 to 5 [i.e. the five model equations developed for the research] were integrated numerically using MATLAB Ode-15 Solver for stiff ordinary differential equations to obtain calculated values of the yields of naphthene, paraffin and aromatic hydrocarbons at the third reactor outlet and the dimensionless reactor temperatures.

An improved estimate of the activation energies were obtained as described in [Senifeld and Lapidus, 1974] according to the model,

$$E_i^{(z+1)} = E_i^{(z)} - \gamma' \left. \frac{\partial S}{\partial E_i} \right|_{E=E_i^{(z)}} \quad [10]$$

The partial differentials  $\frac{\partial S}{\partial E_i}$  were evaluated numerically by varying the activation energy

over a narrow interval (2 KJ Kmol<sup>-1</sup>) about the current values and evaluating the correspondence changes in  $S$ . A suitable upper and lower bound were specified for the activation energies to avoid convergence to some spurious or false values. This aspect was modified applying F-test statistical boundary conditions in the algorithm program. The activation energies of the reactions were estimated to the solving the reactor model [Ojong & Wordu, 2018]; [wordu & Ojong, 2018]. Four major kinetics of the process were coupled with the reactor equations. The reactions models considered were that of the dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffin to naphthenes, cracking of paraffin, and cracking of naphthenes to gases. These reactions were idealized to account for the reforming process.

## SOLUTION TECHNIQUES

### OPTIMAL SEARCH LOGIC - Constrain statistical search model solutions

- $y_{i,cal}$  = computed from ode 45-solver
- $y_{i,plant}$  = obtained from literature (plant design 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.  $\bar{T} = \frac{\sum T}{n}$ ;  $i = P, N, A \& G$
- 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)  

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

$$F_{cal} = \frac{\frac{SSM}{p}}{\frac{SSE}{n-p}} = \frac{MSM}{MSE}$$

Where:

$$\text{Mean of Square Mean [MSM]} = \frac{SSM}{p}$$

$$\text{Mean of Square Error [MSE]} = \frac{SSE}{n-p}$$

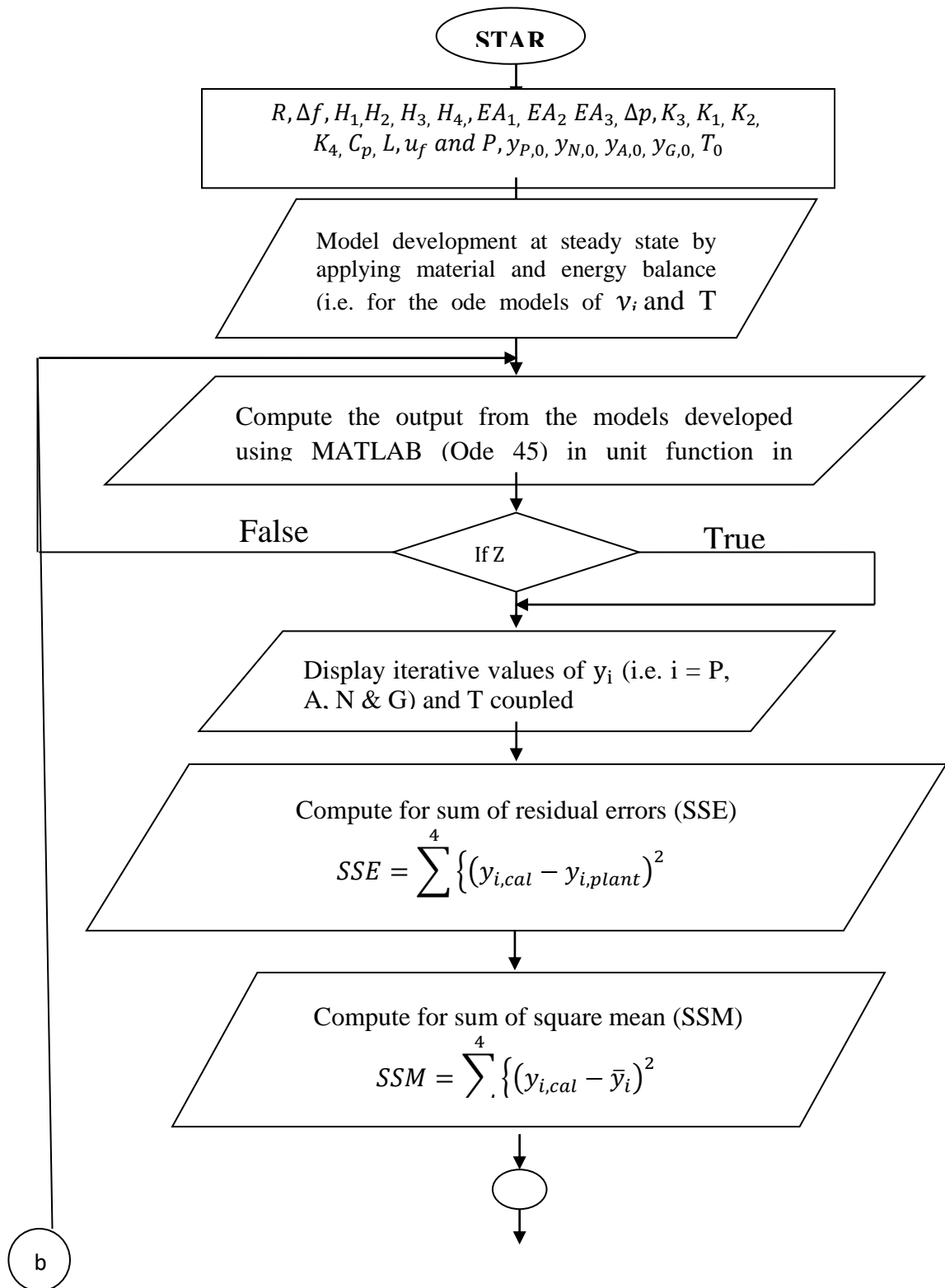
- Compute  $F_{tab}$  from 5% confidence level  
 $1 - \alpha = 1 - 0.05 = 0.95$   
 Degree of freedom of Error =  $n - p$   
 $[DFE] = p - 1$
- Compute for the corrected degree of freedom  
 $DFM = p - 1$   
 $qf = (1 - \alpha, p - 1, n - p)$  i.e.  $qf(0.95, 3, 37)$  for  $n = 41, p = 4$   
 $F_{tab}$  is gotten from table of F – test on range (3, 37) at 95%, 5% confidence level.
- Choose  $\alpha$  such that  $0 < \alpha < 1$   
 $\alpha = 0.85$
- Computer for new Activation Energies  
 $E_i^{j+1} = E_i^j + \alpha \Delta$
- Where increment  $\Delta = -(J_r J_r^T)^{-1} J_r$   
 Where  $J_r = (n \times p)$  Matrix  
 $J_r^T = (p \times n)$  Matrix  
 $\Delta = -[(n \times p)(p \times n)]^{-1}(n \times p)$   
 $i = P, N, A \& G$
- From the  $F_{tab}$ :  
 At 5% confidence level  
 $F_{tab} = 2.911$
- From the  $F_{tab}$  at 10% CL  
 $F_{tab} = 2.278$

**Termination Criterion**

If  $F_C \geq F_{tab}$ , stop iteration else continues till  $F_C \geq F_{tab}$

- Use the updated values of  $E_i$  to obtained the rate constants,  $k_i$   
 $k_i = k_{i,0} \exp\left(\frac{-E_i}{RT}\right)$  From equation [1] above

ALGORITHM OF MATHEMATICAL OPERATIONS



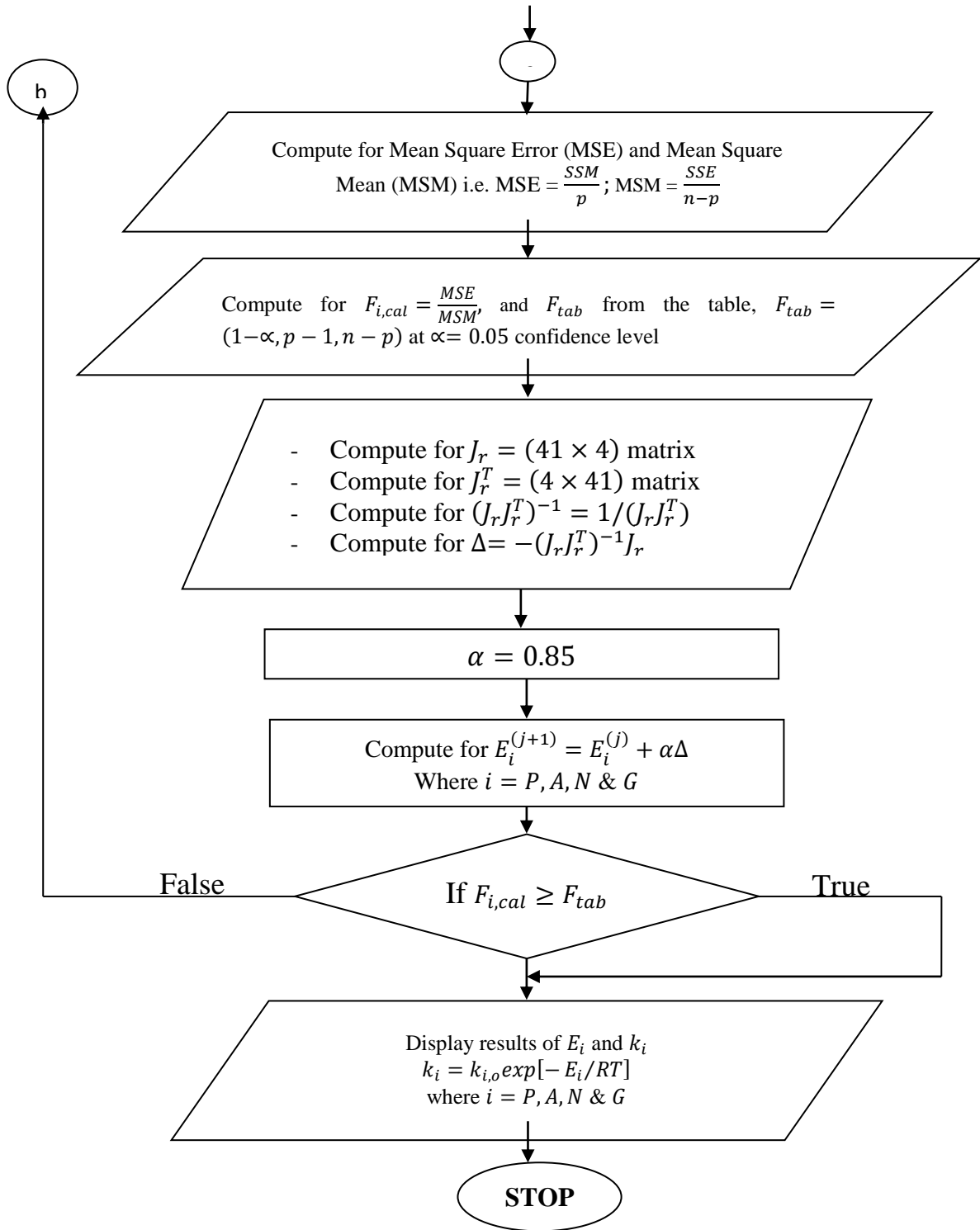


Figure 1 Algorithm for Statistical Search

**PRESENTATION OF RESULTS**

A summary of the search simulation results is given in tables 1 to 7 for clarity. From the tables, the following observations and inferences can be made.

**Table 1 Comparison of estimated Arrhenius constant with literatures**

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 1 depicts the percentage deviation of the pre-exponential factors [Arrhenius constants] literature values. The deviations are reasonable as the approach utilize for the optimization process is a good one.

**Table 2 Results of rate constants calculated from optimal  $E_i$ ,  $A_i$ , &  $T_{o,cal}$  values**

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 2 shows the calculated rate constants from the estimated activation energies, Arrhenius constants and optimal temperature values. The results gave a good estimate of the parameters which can be applied in design and modeling researches.

**Table 3 Comparison of optimum kinetic parameters with literature  $k_i$** 

Parameters	Optimum $k_i$	literature $k_i$	Deviation
<b>Lumps (reformate)</b>	$k_i$	$k_i$	$\% = \left  \frac{\text{OPT. } k_i - \text{Plt } k_i}{\text{Plt } k_i} \right $
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 3 shows the deviation of rate constants of the various species lumps.

**Table 4 Comparison of optimum Yield with Steady State Values**

Parameters	Optimum yield	SSV	Deviation
<b>Lumps (reformate)</b>	<b>Mole</b>	<b>Mole</b>	$\% = \left  \frac{SSV - OY}{SSV} \right $
<b>Paraffins</b>	0.25406	0.26011	2.3
<b>Naphthenes</b>	0.30524	0.29654	2.9
<b>Aromatics</b>	0.60628	0.61208	0.95
<b>Gas</b>	5.8146E-05	5.8544E-05	0.68
<b>Temperature</b>	780.088	780.0815	0.00385

Where: SSV= Steady-State Values

OY = Optimum Yield

Table 4 indicates comparison of the optimal yield with steady state yield. The deviation shows that there is a difference in the two results as optimization procedures gave a better estimates of kinetic parameters to the existing literature values.

**Table 5 Comparison of Optimum Yield with Plant Values**

Parameters	Model Predictions	Plant Data	Deviation
<b>Lumps (reformate)</b>	<b>Mole</b>	<b>Mole</b>	$D = \left  \frac{\text{model} - \text{plant data}}{\text{model}} \right $
<b>Paraffins</b>	0.25406	0.3478	0.26
<b>Naphthenes</b>	0.30524	0.5144	0.41
<b>Aromatics</b>	0.60628	0.1378	3.4
<b>Gas</b>	5.8146E-05	0	-
<b>Temperature</b>	780.088	780	0.00011

Table 5 exhibits comparison of the optimal yield with the literature data. The deviation shows that the estimated kinetic parameters improved literature values. Hence optimization process gave better and enhanced results.

**Table 6 Comparison of Steady State Values with Plant Data**

Parameters	Plant data	SS-values	Deviation
<b>Lumps (reformate)</b>	<b>Mole</b>	<b>Mole</b>	$D = \left  \frac{SSP - \text{Plant data}}{SSP} \right $
<b>Paraffins</b>	0.3478	0.26011	0.25
<b>Naphthenes</b>	0.5144	0.29654	0.42
<b>Aromatics</b>	0.1378	0.61208	3.44
<b>Gas</b>	0	5.854E-05	-
<b>Temperature</b>	780	780.0815	0.0001



Table 5 depicts comparison of the steady state yield and plant data. The deviation indicates the essence of the estimation of kinetic parameters for authenticating accuracy of the method applied in the research by comparing with existing literature values. There is a good prediction of the process models and the algorithm of the optimization is quite reliable and implementable.

### ***Further Results Inferences Presented***

Literature such as 96 iterations, on the activation energies estimated gives values for Naphthene as 174500KJ/Kmol; Aromatics as 356460KJ/Kmol; and Paraffin as 394380KJ/Kmol are available. The values obtain lie within the range quoted in [Smith, 1959] and [Bommann, Srivastava & Saraf, 1989]; [Oboho, 2005]; [Wordu, 2009]; and most recently [Wordu & Ojong, 2018] research values were consistently good with minimum deviations.

The results exhibit 41 iterations on each species P, N, A and G a convergence were achieved making 164 cumulative iterations. This is adjudged correct because of the inclusion of the gas components estimation which was not taken in earlier research works. A comparison on previous literature values on the basis of three components species show that 123 minus 96 iterations gives 26 iterations giving an enhancement on the estimation of the parameters to optimum values.

## **CONCLUSION**

The research springs up a reliable and excellent algorithm technique for the estimation of kinetic parameters of HCs lumps. Furthermore, it brings to bear a clear statistical imaginative tendencies of optimizing kinetic parameters of lumped feed material such as the rate constants forward, backward rate in a reversible reactions and activation energies of chemical reactions taking place in reactors, hence the need to predict  $k$  values and  $E$  values optimally at a particular temperature.

## **NOMENCLATURE**

<b>Symbols</b>	<b>Meaning</b>	<b>Units</b>
$E_a$	Activation Energy	$J/Kmol$
$\Delta H$	Enthalpy Change	
$R$	Gas constant	$KJ/Kmol K$
$K^+$	Rate constant	
$A$	Pre-exponential factor/frequency factor or Arrhenius constant $A_0$ or $K_0$	
$y_i$	Mole fraction of species, $i$	$i$
SS	Sum of squares	
$R^2$	Coefficient of determination	
CL	Confidence limit	
$\lambda$	Marquarrett-Levenberg parameter	
$\Delta$	Incremental value	

$P_i$	Partial pressure of species, $i$	$kp_a$
$\tau$	Space Time,	$s$
$C_T$	Total concentration	$mol/m^3$
$P_{ESS}$	Pure Error Sum of Squares	
$y_i$	Mole fraction of species $i$ , where $i =$ Naphthenes, Paraffins, Aromatics	
$RSS$	Regression Sum of Square	
$V_o$	Volumetric flow,	$m^3/s$
$\Delta H_{r,i}$	Change in Heat of Reaction of species, $i = N, P, A \& G$	$KJ/Kmol$
$Q$	Quantity of heat,	$KJ/s (KW)$
$q$	Quantity of heat per unit volume	$KW/m^3$
$C_p$	Specific heat capacity of the system	$KJ/Kmol K$
$u_f$	Superficial velocity,	$m/s$
$K_p$	Equilibrium constant,	$KJ/Kmol$
$K_f$	Rate constant of forward reaction	
$k_r$	Rate constant of reverse reaction	
$y_N$	= mole fraction of Naphthenes, mol	
$y_A$	= mole fraction of Aromatics; mol	
$y_P$	= mole fraction of paraffins, mol	
$y_{H_2}$	= mole fraction of Hydrogen; mol	
$r_i$	= rate of reaction for species, $i$ , = $[N, A, P, H_2, \text{and } G]$ ; mol/s	

$K_{i,j}$  = Rate constant for the four reactions

$A_{oi,j}$  = Frequency or pre-exponential factor or constant.

$E_{i,j}$  = Activation energy of the reactions

$R$  = Universal gas constant

$T$  = Absolute K

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