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Kinetic Parameters of Feed-Lumps for Reforming Reactors

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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. The results of the activation energies are stated explicitly as E_i 354950KJ/Kmol; 173566KJ/Kmol; 395001KJ/Kmol and 394005KJ/Kmol of P, N, A & G species respectively. The optimal E_i -values gave updated k_i -values of 5.63E-12; 2.46E-04; 1.76E-08 and 1.56E-08 of P, N, A & G. The deviations 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. And, the values can be applied for any design and modeling research works.

Keywords: Kinetic parameters, lump-feed, activation energies, optimum-search

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 [functions of activation energies in 5-lump reactor model] which is to be minimized or a reward function or utility function to be maximized [Wenyu & Ya-Xiang, 2010]. 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.

Many unconstrained optimization algorithms can be adapted to the constrained case, often through the use of a penalty method. However, search steps taken by the unconstrained method may be unacceptable for the constrained problem, leading to a lack of convergence which is referred to as the maratos effect.

Another solution technique for constrained optimization is the equality constraints. Here the method of Lagrange multipliers can be used to convert it into an unconstrained problem whose number of variables is the original number of variables plus the original number of equality constraints. Alternatively, if the constraints are all equality constraints and are all linear, they can be solved for some of the variables in-terms of the others and the former can be substituted out of the objective function, leaving an unconstrained problem in a smaller number of variables. Inequality constraints problem can be characterized in-terms of geometric optimality conditions, Fritz John conditions and Karush-Kuhn-Tucker conditions in which simple problems may be solved.

Programming method for constrain optimization is one of the vital methods in this research in which linear and quadratic programming techniques applicable to polynomial can be solved by simplex method.

[Yucer, 2005] developed a parameter estimation software named PARES [Parameter Estimation] coded in MATLAB 6.5 to determine the values of model parameters that provide the best fit to measured data, based on some type of least squares or maximum likelihood criterion.

The statistics and kinetics take the form of a set of differential algebraic equations and formulation of these parameters estimation problem are well studied. Mathematical formulation of chemical reaction mechanisms was taken as exemplary systems to demonstrate the optimization algorithm, given by a coupled system of stiff nonlinear differential equation [1] below.

$$\frac{dy}{dt} = f(t, y, p) \quad y(t^0) = y^0; \quad t^0 \leq t \leq t^t \quad [1]$$

Where y is the state vector of the system, P is the model parameters.

The figure[1] below shows the logic flow diagram for the parameter estimation algorithm developed, which has been extensively tested before with a number of different problems [Agun, 2002]. The algorithm offers the possibility of employing different numerical optimization routines with ease to estimate the updated P in order to satisfy the particular needs of the model employed.

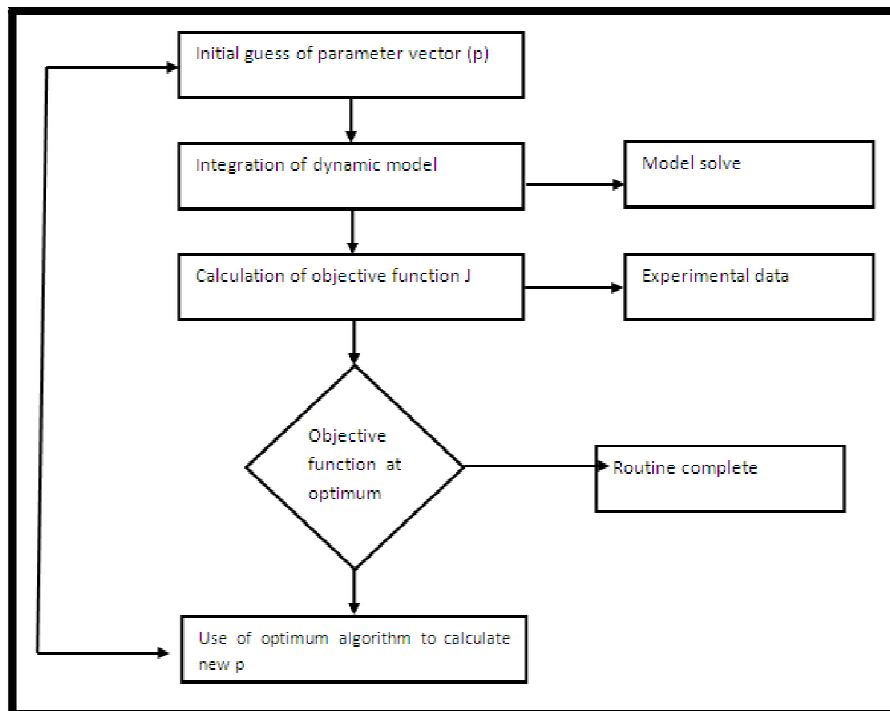


Figure 1: Iteration Process for Parameter Estimation [Agun, 2002]

[Wordu, 2009]doctoral thesisdynamic simulation of industrial reformer reactor [DSIRR]; and [Oboho, 2005]estimation of kinetic parameters to simulate catalytic reactor block. Models on material and energy balance were developed which expressed the kinetic parameters of Activation energies, E_i ,rate constants forward and reverse reactions process and equilibrium constant of the feeds cracking reactions in the reactors.

The constants were determined using optimization search especially activation energies of the lumps. The research objective function, S was the sum of the squares of the difference between the calculated and experimental values of mole fractions of the various lumps and dimensionless reactor outlet temperature.

$$S = \sum_i^m \left[\left\{ \sum_{i=1}^3 (N_{i,cal} - N_{i,plant})^2 + \sum_{j=1}^3 (T_{i,cal} - T_{i,plant})^2 \right\} \right] \quad [2]$$

Where,

m = number of data sets used.

$i = 1, 2$ and 3 for Naphthene, Paraffins and Aromatics Hydrocarbon respectively.

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

To achieve this, the five models developed from the reaction of reforming feed naphtha were solved numerically using mat lab ode 15s solver to obtain calculated values of the yields of naphthene, paraffin and aromatic hydrocarbons at the third reactor outlet and the dimensionless reactor temperatures.

The improved activation energies were gotten by applying the objective function model to the model according to [Senifeld & Lapidus, 1974] below:

$$E_i^{(z+1)} = E_i^{(z)} - \gamma \left. \frac{\partial S}{\partial E_i} \right|_{E=E^z} \quad [3]$$

The partial differentials, $\frac{\partial S}{\partial E_i}$ was evaluated numerically by boundary conditions of activation energy narrow interval of 2KJ/Kmol about the current values and evaluating the corresponding changes in S .

[Erick & Gustavo, 2006]researched on estimation of activation energies using hydrodesulphurization of middle distillates.[Raghuna-than& Yang, 1996]posited a doctoral thesis on estimation of activation energies coal gasification reaction process.

2. Materials and Method

2.1. Materials

The materials applicable are the feed naphtha, reformer reactors, optimization model search [direct-search method, least squares regression model], Marquardt-Levenberg algorithm,thermodynamic model and data ,derivation of appropriate materials and energy balance models.

2.2. Method

2.2.1. Continuous Catalyst Cracking Reactor Model [CCCRM][Wordu & Ojong, 2018]

2.2.1.1. Theoretical Concepts

2.2.1.1.1. Constraints/Assumptions for Model Development

The derivation of the reactor model for this research maintains these constraints/ assumptions:

- There is continuous catalyst regeneration in the regenerator unit section of the reactor which keeps the catalyst at 100% efficiency.
- The reactor is a 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 C₆ – C₈ hydrocarbons
- Models maintain a lumping scheme chemistry of the paraffin, aromatics and naphthene.
- Hydrogen recycle shall maintain 1.6 moles

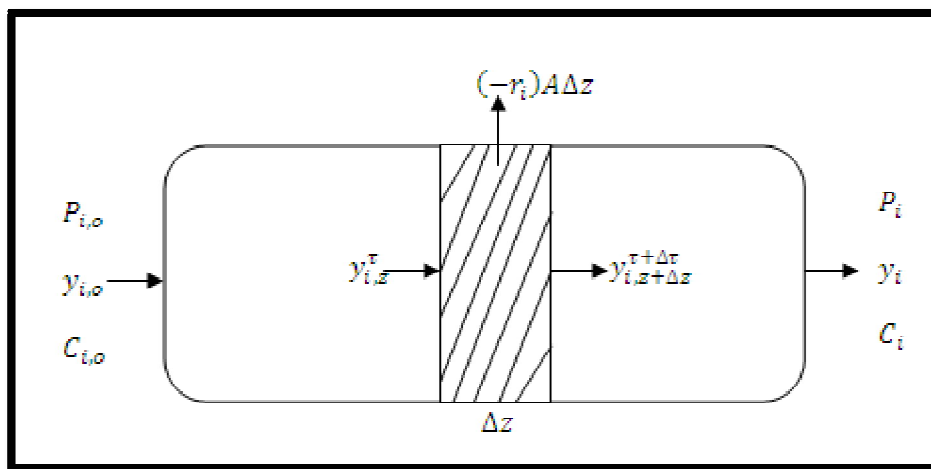


Figure 2: Schematics of Ideal Plug Flow Reactor Differential Volume Dv .

Explicitly, the fundamental material balance for 1 mole of feed is stated below;

$$Au_f C_i \Big|_z^\tau - Au_f C_i \Big|_{z+\Delta z}^{\tau+\Delta\tau} + (-r_i)A\Delta z = 0 \quad [4]$$

$$Au_f C_i \left[\Big|_{z+\Delta z}^{\tau+\Delta\tau} - \Big|_z^\tau \right] + (-r_i)A\Delta z$$

Equation [4] is developed under steady state process;

$$\left\{ \begin{array}{l} \text{Rate of accumulation} \\ \text{of species, i, within the} \\ \text{reactor} \end{array} \right\} = 0 \quad [5]$$

$$\left\{ \begin{array}{l} \text{Rate of inflow of} \\ \text{species, i, in the} \\ \text{flow reactor} \end{array} \right\} = v_o C_{i,z}^\tau \quad [6]$$

$$\left\{ \begin{array}{l} \text{Rate of outflow of} \\ \text{species, i, from the} \\ \text{flow reactor} \end{array} \right\} = v_o C_{i,z+\Delta z}^{\tau+\Delta\tau} \quad [7]$$

$$\left\{ \begin{array}{l} \text{Rate of depletion} \\ \text{of species, i, due to} \\ \text{chemical reaction} \\ \text{processes occurring} \\ \text{within the flow reactor} \end{array} \right\} = (-r_i)\Delta V \quad [8]$$

Combining equations (5) to (8) into equation (4) yields the material balance model equation [9].

$$\frac{dn}{d\tau} = v_o C_{i,z}^\tau - v_o C_{i,z+\Delta z}^{\tau+\Delta\tau} - (-r_i)\Delta V \quad [9]$$

$$\frac{d(VC_i)}{d\tau} = v_o [C_{i,z+\Delta z}^{\tau+\Delta\tau}] - (-r_i)A\Delta Z$$

$$\frac{\partial(C_iAz)}{\partial\tau} = v_o\Delta C_i - (-r_i)A\Delta Z$$

$$A\Delta Z \frac{\partial C_i}{\partial\tau} = v_o\Delta C_i - (-r_i)A\Delta Z$$

Divide both sides by $\Delta Z A$

$$\frac{\partial C_i}{\partial\tau} = -\frac{v_o}{A} \frac{\Delta C_i}{\Delta Z} - (-r_i)$$

$$\lim_{\Delta z \rightarrow 0} \frac{\Delta C_i}{\Delta z} = \frac{\partial C_i}{\partial z} \quad [10]$$

$$\frac{\partial C_i}{\partial\tau} = -\frac{v_o}{A} \frac{\partial C_i}{\partial z} - (-r_i)$$

$$\frac{\partial C_i}{\partial\tau} + \frac{v_o}{A} \frac{\partial C_i}{\partial z} + (-r_i) = 0 \quad [11]$$

But,

$$y_i = \frac{C_i}{C_T} = P_i/P_T$$

But

From ideal gas equation

$$C_i = P_i/R_T \quad [12]$$

Thus:

$$\frac{\partial C_i}{\partial\tau} + \frac{v_o}{A} \frac{\partial C_i}{\partial z} + (-r_i) = 0$$

$$\frac{1}{RT} \frac{\partial P_i}{\partial\tau} + \frac{v_o}{ART} \frac{\partial P_i}{\partial z} + (-r_i) = 0 \quad [12]$$

$$\frac{\partial P_i}{\partial\tau} + \frac{v_o}{A} \frac{\partial P_i}{\partial z} + RT(-r_i) = 0 \quad [13]$$

Again, from Roault's law of partial pressures;

$$y_i = P_i/P_T$$

$$P_i = P_T y_i \quad [14]$$

$$P_T \frac{\partial y_i}{\partial\tau} + P_T \frac{v_o}{A} \frac{\partial y_i}{\partial z} + RT(-r_i) = 0$$

$$\frac{\partial y_i}{\partial\tau} + \frac{v_o}{A} \frac{\partial y_i}{\partial z} + \frac{RT}{P_T} (-r_i) = 0$$

$$\frac{\partial y_i}{\partial\tau} + \frac{v_o}{A} \frac{\partial y_i}{\partial z} + C_T (-r_i) = 0 \quad [15]$$

At steady state; $\frac{\partial y_i}{\partial\tau} = 0$

$$\frac{v_o}{A} \frac{dy_i}{dz} + C_T (-r_i) = 0 \quad [16]$$

But,

$$\frac{v_o}{A} = \frac{F_{Ao}}{A} = L/\tau = u_f \quad [17]$$

$$u_f \frac{dy_i}{dz} + C_T (-r_i) = 0 \quad [18]$$

Equation [18] is the model for the material balance

2.3. Kinetic Model

Development of the kinetic lumps: [Naphtha, Paraffins, Aromatics and Gases [C₁, C₂, C₃ & C₄].

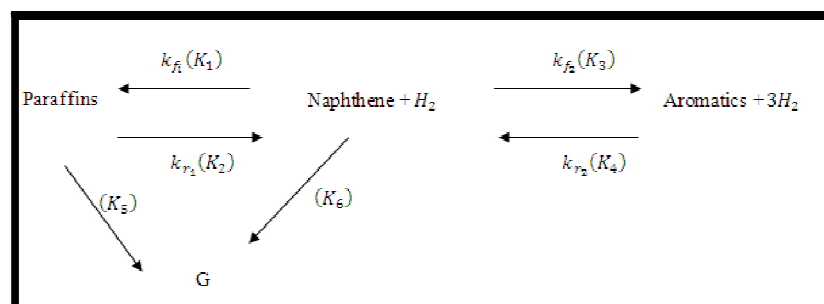


Figure 3: Lumps Model of Reforming Reactions [Oboho, 2005]; [Wordu, 2009]

[Jacob & Weekman, 1976]; [Coxon & Bischoff, 1987]; and most recently [Obobo, 2005]; [Wordu, 2009] posited that the reactions taking place in the reactors follow lumping scheme kinetics shown in figure 3. According to [Obobo, 2005]; [Wordu, 2009], the rate expressions for the composite 5-lumps kinetics is given below as:

$$(-r_N) = -k_{r_1} P_P + k_{f_1} P_N P_{H_2} + k_{f_2} P_N P_{H_2} - k_{r_2} P_A P_{H_2}^3 + k_6 P_N P_{H_2} \quad [19]$$

Expressing equation [3.16] in terms of mole fractions (y_i) and Defining equilibrium constant, k_p

$$k_p = \frac{k_f}{k_r} \quad [20]$$

Equation [19] becomes:

$$\begin{aligned} (-r_N) &= -C_T \frac{dy_N}{d\tau} = k_{f_1} P_T^2 y_N y_{H_2} + k_{f_2} P_T^2 y_N y_{H_2} + k_6 P_T^2 y_N y_{H_2} \\ &\quad - k_{r_1} P_T y_P - k_{r_2} P_T^4 y_A y_{H_2}^3 \\ (-r_N) &= (k_{f_1} + k_{f_2} + k_6) P_T^2 y_N y_{H_2} - \frac{k_{f_1}}{k_{P_1}} P_T y_P - \frac{k_{f_2}}{k_{P_2}} P_T^4 y_A \end{aligned} \quad [21]$$

$$\begin{aligned} (r_A) &= C_T \frac{dy_A}{d\tau} = k_{f_2} P_T^2 y_N y_{H_2} - k_{r_2} P_T^4 y_A y_{H_2}^3 \\ &= k_{f_2} P_T^2 y_N y_{H_2} - \frac{k_{f_2}}{k_{P_2}} P_T^4 y_A y_{H_2}^3 \end{aligned} \quad [22]$$

$$\begin{aligned} (-r_P) &= -C_T \frac{dy_P}{d\tau} = k_{r_1} P_T y_P - k_{f_1} P_T^2 y_N y_{H_2} + k_5 P_T y_P \\ &= \frac{k_{f_1}}{k_{P_1}} P_T y_P - k_{f_1} P_T^2 y_N y_{H_2} + k_5 P_T y_P \\ &= \left(\frac{k_{f_1}}{k_{P_1}} + k_5 \right) P_T y_P - k_{f_1} P_T^2 y_N y_{H_2} \end{aligned} \quad [23]$$

$$\begin{aligned} (r_{H_2}) &= \frac{dy_{H_2}}{d\tau} = k_{r_1} P_T y_P - k_{f_1} P_T^2 y_N y_{H_2} - k_6 P_T^2 y_N y_{H_2} \\ &\quad - (k_{f_2} + k_{r_2}) P_T^2 y_N y_{H_2} + (k_{f_2} - k_{r_2}) P_T^4 y_A y_{H_2}^3 \\ &= \frac{K_{f_1}}{K_{P_1}} P_T y_P - K_{f_1} P_T^2 y_N y_{H_2} - K_6 P_T^2 y_N y_{H_2} - K_{f_2} P_T^2 y_N y_{H_2} + \frac{k_{f_2}}{k_{P_2}} P_T^2 y_N y_{H_2} \\ &\quad + k_{f_2} P_T^4 y_A y_{H_2}^3 - \frac{k_{f_2}}{k_{P_2}} P_T^4 y_A y_{H_2}^3 \end{aligned}$$

$$(r_{H_2}) = \frac{k_{f_1}}{k_{P_1}} P_T y_P + \left(\frac{k_{f_2}}{k_{P_2}} - k_{f_1} - k_6 - k_{f_2} \right) P_T^2 y_N y_{H_2} + \left(k_{f_2} - \frac{k_{f_2}}{k_{P_2}} \right) P_T^4 y_A y_{H_2}^3 \quad [24]$$

$$(r_G) = C_T \frac{dy_G}{d\tau} = k_5 P_T y_P + k_6 P_T^2 y_N y_{H_2} - k_7 P_T y_G \quad [25]$$

2.4. Energy Balance [Temperature Model Development]

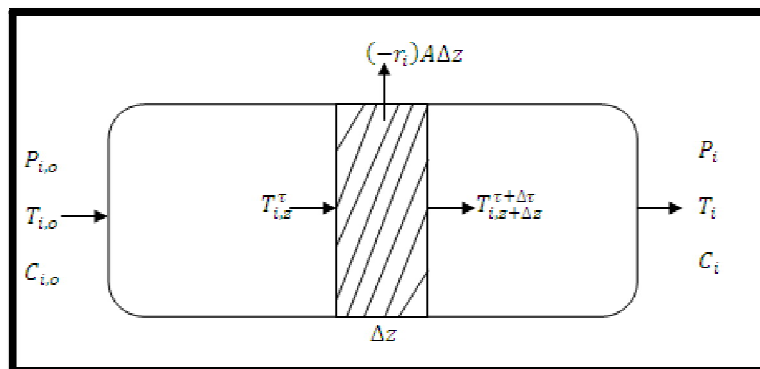


Figure 4: Elemental Volume PFR Showing Temperature Variations in the Z-Direction

For 1 mole of a lumped feed into the reactor, the energy/temperature balance is explicitly stated below. Energy balance is stated mathematically at steady-state process

$$v_0 \rho C_p A T_i \Big|_z^\tau - v_0 \rho C_p A T_i \Big|_{z+\Delta z}^{\tau+\Delta\tau} + (-r_i)(-\Delta H_R)A\Delta z - Q\Delta\tau = 0$$

$$\rho C_p A T_i \left[\Big|_{z+\Delta z}^{\tau+\Delta\tau} - \Big|_z^\tau \right] + (-r_i)(-\Delta H_R)A\Delta z - Q\Delta\tau = 0$$

Input - Output + Reaction = Accumulation

$$\{Rate\ of\ Accumulation\} = 0$$

[26a]

[26b]

$$\left\{ \begin{array}{l} \text{Rate of inflow of} \\ \text{energy into the} \\ \text{differential volume} \end{array} \right\} = v_o \rho A C_p T_{i,z}^T \quad [27]$$

$$\left\{ \begin{array}{l} \text{Rate of outflow of energy} \\ \text{of species, i from the differential} \\ \text{element of volume} \end{array} \right\} = v_o \rho A C_p T_{i,z+\Delta z}^{T+\Delta T} \quad [28]$$

$$\left\{ \begin{array}{l} \text{Rate of depletion of energy} \\ \text{of species, i, within the} \\ \text{differential element of} \\ \text{volume of the reactor} \end{array} \right\} = (-r_i)(-\Delta H_r) A \Delta z \quad [29]$$

$$\left\{ \begin{array}{l} \text{Rate of energy added into the} \\ \text{differential volume of element} \\ \text{of the flow reactor} \end{array} \right\} = Q \Delta \tau \quad [30]$$

Combining equations [26b] to [30] into equation [26a] [31]

$$0 = -v_o \rho C_p A (T_{i,z+\Delta z}^{T+\Delta T} - T_{i,z}^T) - (-r_i)(-\Delta H_{r_i}) \Delta z A + Q \Delta \tau \quad [32]$$

At Adiabatic conditions; $T_i = T_c$,

$$\text{Hence: } Q = UA(T_i - T_c) = 0$$

And, equation [32] becomes:

$$0 = -v_o \rho C_p A \Delta T(\tau, z) - (-r_i)(-\Delta H_{r_i}) \Delta z A \quad [33]$$

Divide equation (3.31) by $v_o \rho C_p A \Delta z$

$$\frac{\Delta T_i(\tau, z)}{\Delta z} + \frac{(-r_i)(-\Delta H_{r_i})}{v_o \rho C_p} = 0$$

But

$$\lim_{\Delta z \rightarrow 0} \frac{\Delta T(\tau, z)}{\Delta z} = \frac{dT}{dz}$$

Thus;

$$\frac{dT}{dz} + \frac{(-r_i)(-\Delta H_{r_i})}{u_f \rho C_p} = 0 \quad [34]$$

Where: r_i = rate of reaction for species, $i = (N, A, P, H_2, \text{ and } G)$; mol/s

Equation [34] is the temperature model for reformer reactors.

Equation [34] can further be analyzed/expressed as:

$$\frac{dT}{dz} + \frac{1}{u_f \rho C_p} \left((-r_N)(-\Delta H_N) + (-r_A)(-\Delta H_A) + (-r_P)(-\Delta H_P) + (-r_{H_2})(-\Delta H_{H_2}) \right) = 0$$

$$\frac{dT}{dz} + \frac{1}{u_f \rho C_p} \left((-r_N)(-\Delta H_N) + (r_A)(\Delta H_A) + (-r_P)(\Delta H_P) + (r_{H_2})(\Delta H_{H_2}) + (r_G)(\Delta H_G) \right) = 0 \quad [35]$$

Reactions 1, 2, 3 & 4	A_o	Equation constant (K_p)	$\Delta H_R \frac{KJ}{Kmol}$ of H_2 liberated
Conversion of naphthenes to aromatics	1.19×10^8	$1.040 \times 10^6 \exp \left[46.15 - \frac{212700}{RT} \right]$	70928
Conversion of paraffins to naphthenes	4.170×10^{13}	$9.869 \times 10^3 \exp \left[\frac{36950}{RT} - 712 \right]$	-44185
Naphthenes cracking	4.5881×10^{18}	—	-51860
Paraffin cracking	4.5881×10^{18}	—	-51860

Table 1: Kinetic Parameter A_o , K_p , K_f , K_c & ΔH_R [Wordu, 2009] Input Data

3. Solution Techniques

The various differential equations are resolved using 4th Order Runge-Kutta numerical method. Algorithm for the optimization of the kinetic parameters is given in figure 5 below:

Computational flow chart: Mechanism/kinetics [CCCR]

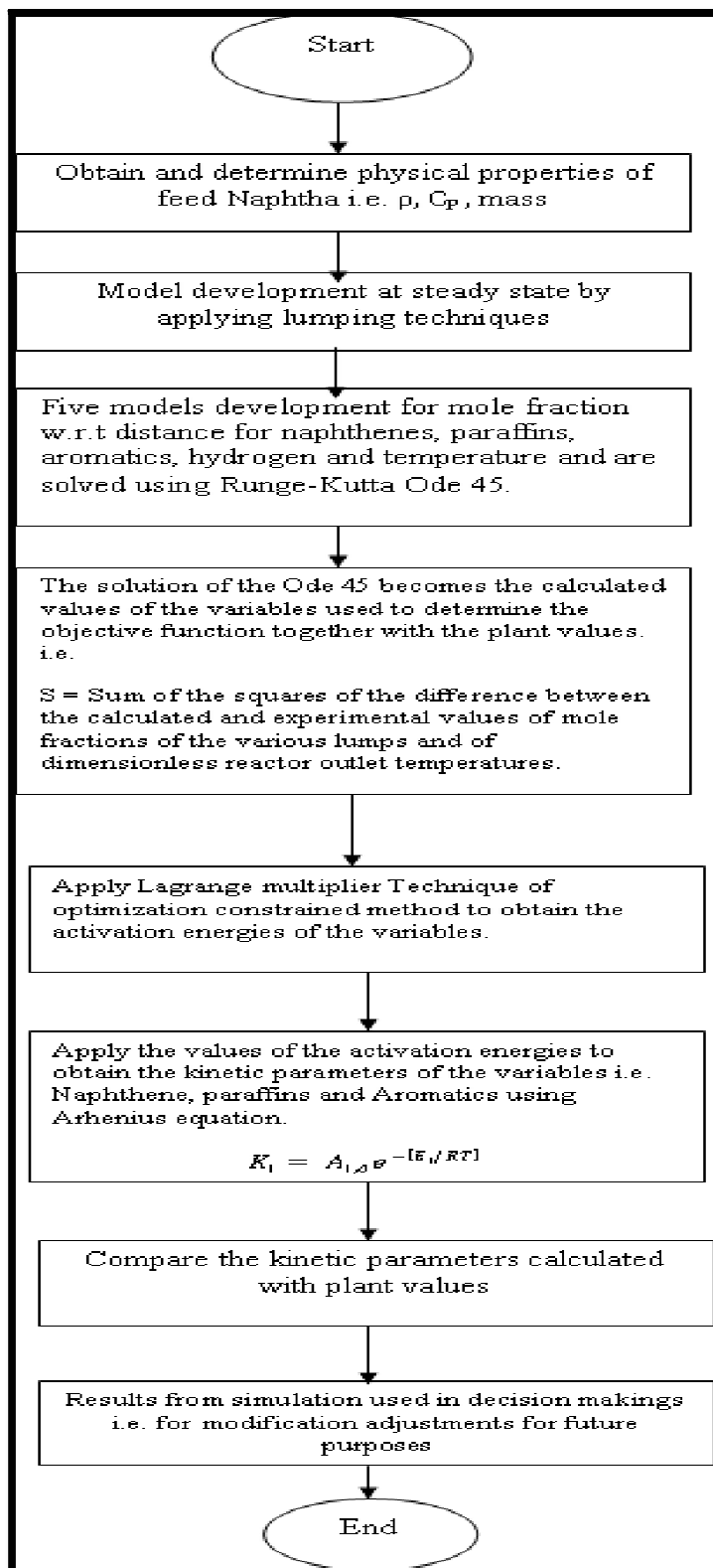


Figure 5: Algorithms for Mechanism and Kinetics

3.1. 4th Order Runge- Kutta Numerical Algorithm for Systems of Ordinary Differential Equations

$$\frac{dT}{dz} = \frac{1}{\mu_f} (-r_i) \quad [36]$$

$$\frac{dT}{dz} = \frac{1}{\mu_f C_{PP}} \left\{ \sum_{i=1}^5 (-r_i) (\Delta H_{r,i}) \right\} \quad [37]$$

Equations [36] and [37] are assigned 1 and 2 respectively for the Algorithm below:

$i = P, N, A, H_2 \text{ and } G$

$$K_{11} = hf(z_j, y_{i,j}; T_j)$$

$$K_{12} = hf(z_j, y_{i,j}; T_j)$$

$$K_{21} = hf(z_j + \frac{1}{2}h; y_{i,j} + \frac{1}{2}K_{11}h; T_j + \frac{1}{2}K_{12}h)$$

$$K_{22} = hf(z_j + \frac{1}{2}h; y_{i,j} + \frac{1}{2}K_{11}h; T_j + \frac{1}{2}K_{12}h)$$

$$K_{31} = hf(z_j + \frac{1}{2}h; y_{i,j} + \frac{1}{2}K_{21}h; T_j + \frac{1}{2}K_{22}h)$$

$$K_{32} = hf(z_j + \frac{1}{2}h; y_{i,j} + \frac{1}{2}K_{21}h; T_j + \frac{1}{2}K_{22}h)$$

$$K_{41} = hf(z_j + h; y_{i,j} + K_{31}h; T_j + K_{32}h)$$

$$K_{42} = hf(z_j + h; y_{i,j} + K_{31}h; T_j + K_{32}h)$$

$$\Delta y_{i,j} = \frac{1}{6} \{K_{11} + 2K_{21} + 2K_{31} + K_{41}\}$$

$$\Delta T_j = \frac{1}{6} \{K_{12} + 2K_{22} + 2K_{32} + K_{42}\}$$

$$y_{i,j+1} = y_{i,j} + \Delta y_{i,j}$$

$$T_{j+1} = T_j + \Delta T_j$$

$$z_{j+1} = z_j + h$$

Notations for Runge-Kutta numerical method

$$j = 0, 1, 2, \dots, n-1$$

$$h = \text{stepsize}$$

$$\Delta y_{i,j} = \text{slope of the mole fraction of species } i \text{ at the } j \text{ - iteration.}$$

$$\Delta T_j = \text{slope of the Temperature at } j \text{ iteration}$$

1, 2 = prefix indicating equations for mole fraction and temperature respectively.

3.2. Program Step Wise Sequence for Parameter Estimation of Components by Gauss-Newton & Marquardt- Levenberg Method

By adopting the least square regression iterative procedures to update the activation energies of paraffins, naphthenes, aromatics & hydrogen values of the species given, the kinetic parameters of the species are estimated viz:

Step 1: The computation of the yields of the mole fraction and temperature values from the model equations obtained as a result of the Rate expressions derived from five-lump Complex reactions using Ode 45-solver. The model equations derived are set of ordinary differential equations at steady state of plug flow reactor material and energy balances.

Step 2: The yield of mole fractions and temperature obtained from the Ode-45-solver are compared with the plant data/literature values of the mole-fractions and temperature of the species: paraffins, naphthenes, aromatics and hydrogen is then used to compute the objective function, S, since:

$$S = \sum_{i=1}^5 \left\{ \sum_{i=1}^5 (y_{i,cal} - y_{i,pt})^2 + \sum_{i=1}^5 (T_{0,cal} - T_{0,pt})^2 \right\} \quad [38]$$

Where: $y_{i,cal}$ is mole fractions. Values obtained from Ode 45 solver for species

$$i = P, N, A, \text{ and } H$$

$y_{i,pt}$ is mole fractions values obtained from the literature/plant data and are initial values for the simulations: i.e.

$$y_{P,0} = 0.3478; y_{N,0} = 0.5144$$

$$y_{A,0} = 0.1378 \text{ \& } y_{H_2,0} = 8$$

$T_{0,cal}$ = Temperature values obtained from Ode-45-solver

$T_{0,cal}$ is initial Temperature value obtained from literature or plant and is

$$T_{0,pt} = 780K$$

Step 3: Since the mole fraction obtained is a function of distance, z along the reactor and the activation energies i.e. $y_i = f(z, E_i)$; then: $E_i = (E_1, \dots, E_5)$ where: 1 = P, 2 = N, 3 = A, 4 = H_2 & 5 = G

are the kinetic parameters of the model that we are trying to find to minimize S

Step 4: Starting with the initial guess, $E_i^{(0)}$, the Gauss-Newton algorithm will iteratively find the best values for E_i as follows:

$$(i) \quad E_i^{(s+1)} = E_i^{(s)} + \alpha \Delta$$

Where Δ = increment vector given as: $\Delta = -(J_r^T J_r)^{-1} J_r$

$$\text{Where: } (J_r)_{i,j} = \frac{\partial r_i(E_i)}{\partial E_i}$$

Suffix: T = Transpose of the matrix vector

-1 = Inverse of the matrix product of $J_r^T J_r$, α = Constant used when the yields of the experimental data (calculated mole fraction values) of the mole fraction are becoming relatively steady as in my thesis;

Then, $\alpha > 0$ and the optional value for α can be determined by line-search algorithm i.e. using a direct-search method in the interval: $0 < \alpha < 1$.

Note the Δ can be thought as the correction applied to E_i to get it closer to the solution [value of E_i that will give the least minimal value of S, the objective function for series of iterations].

Update the parameter values, $E_i^{(z11)}$ for the species, i to minimize the objective functions, S, this step 4 is majorly gotten with optimization package i.e search that give best convergence.

4. Results and Discussions

The results are presented in tables 1, 2, 3, 4, 5 and figures 1, 2, 3, 4, 5 for clarity.

The optimization algorithm flow scheme figure 7 adapts mat lab compiler to simulate the models to give steady states and optimal yields of the mole fractions of the HCs lump feeds. Steady state results obtained were subjected to

optimization process to estimate the kinetic parameters of activation energies and pre-exponential factors. Results are presented below in tables and figures below for discussions.

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 2: Comparison of Estimated Arrhenius Constant with Literatures Values

Table 2 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.

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 3: Results of Rate Constants Calculated from Optimal E_i , A_i , & $T_{o,cal}$

Table 3 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 when compared with literature values [Wordu, 2009].

Parameters	Optimum k_i	literature k_i	Deviation
Lumps (reformate)	k_i	k_i	$\% = \left \frac{OPT. k_i - Pltk_i}{Pltk_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 4: Comparison of Optimum Kinetic Parameters with Literature k_i from Table 1

Table 4 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.

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

Table 5: Comparison of Optimum Yield with Steady State Values

Where: SSV= Steady-State Values

OY = Optimum Yield

Table 5 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.

Parameters	Model Predictions	Plant Data	Deviation
Lumps (reformate)	Mole	Mole	$D = \frac{ \text{model} - \text{plantdata} }{\text{model}}$
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 6: Comparison of Optimum Yield with Plant Data

Table 6 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).

Parameters	Plant data	SS-values	Deviation
Lumps (reformate)	Mole	Mole	$D = \frac{ SSP - \text{Plantdata} }{SSP}$
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 7: Comparison of Steady State Values and Plant Data

Table 7 depicts comparison of the steady state yield and plant data. The deviation indicates the essence of the estimation of kinetic parameters, but the deviations are small indicating the accuracy of the method applied in the research for the results.

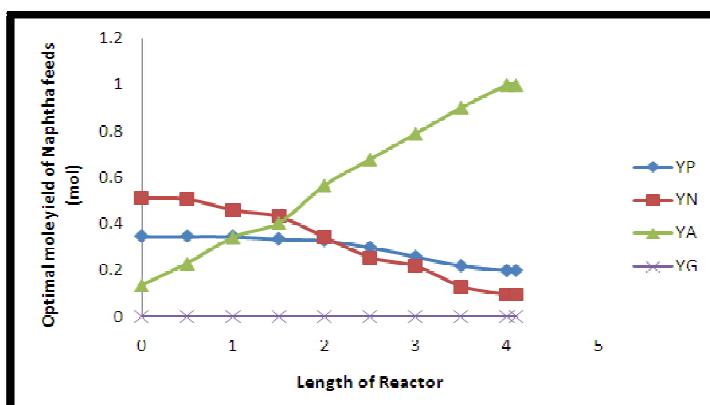


Figure 6: Optimal Mole Fractions Yields Varying With Reactor Length [M]

Figure 6 depicts optimal yield of mole fractions for the species [P, N, A, and G] of feed with the reactor length. The result shows that there is progressive increase in mole fractions of aromatics and gas. The point of intersection signifies equilibrium of the feed cracking process and tends to spread out to maximum as the reactor length increased to maximum.

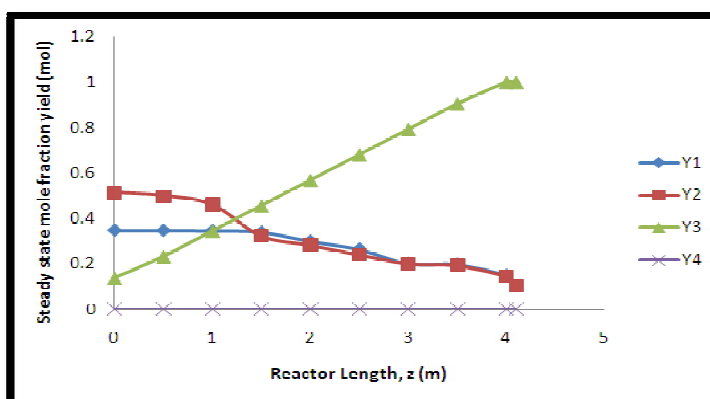


Figure 7: Steady State Yield of Mole Fraction of Feeds versus Reactor Length [M]

Figure 7 shows the steady state yields of mole fractions of the species [P, N, A, and G] of lump feed varying along the reactor length. The figure 7 show naphthene and paraffin depletes effectively to give products of gases and aromatics gasoline. The steady state models gave better yields and models purpose was achieved.

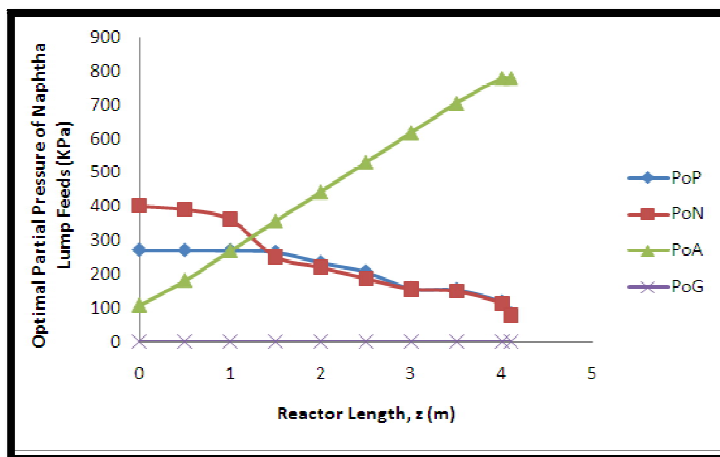


Figure 8: Optimal Partial Pressures of Feeds Varying with Reactor Length [M]

Figure 8 indicates the optimal yield of various species of the lumped feed in terms of partial pressures (kPa) with the reactor length as a mark of consistency. From figure 8, immediately after equilibrium point there is a good overlap of paraffin and naphthene depletion process testifying good model performance.

The optimal values are gotten from the estimated kinetic parameters (E_i and A_i), which were subjected to optimization process. The yields show that P_A and P_G increase as reactor length increases such that $P_A > P_G$ indicating that more of aromatics and gases are produced in the reactors. While the partial pressure of paraffins and Naphthenes decreases from initial value as length of reactor increased to maximum. This is because the partial pressure of paraffins initially depletes to give Naphthenes and Gas, and Naphthenes depletes to give aromatics and gases $C_1 - C_4$ fractions. A brief mathematical analysis states simply: At $z=0m$, $P_p = 271.284 kPa$, $P_N = 401.232 kPa$, $P_A = 107.484 kPa$ and $P_G = 0 kPa$, and at $z = 4m$, $P_p = 117 kPa$, $P_N = 113.1 kPa$, $P_A = 780 kPa$ and $P_G = 0.0839 kPa$ QED

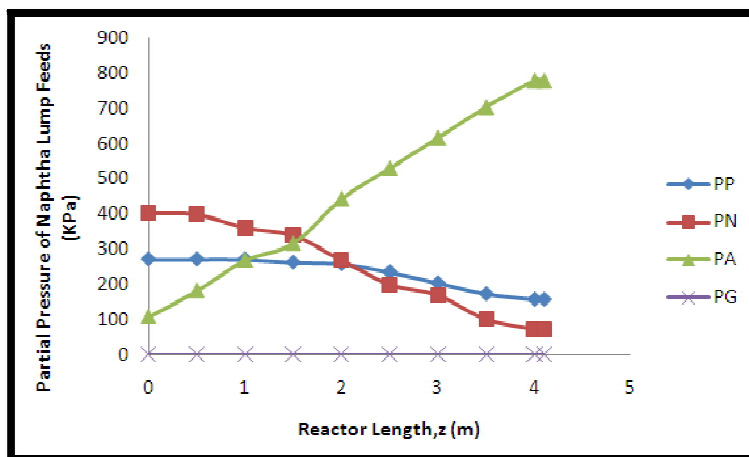


Figure 9: Steady State Partial Pressure of Feed With Reactor Length [M]

Figure 9 depicts the steady state partial pressure of lumped feed (kPa) varying with the reactor length (z).

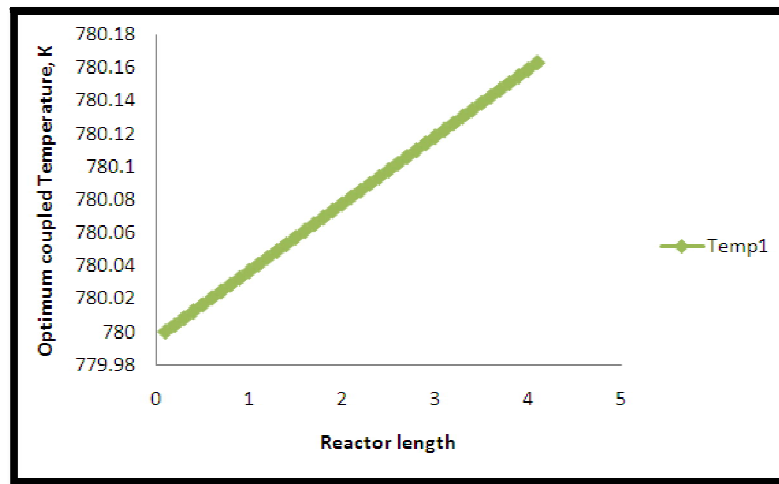


Figure 10: Optimum Temperatures against Reactor Length [m]

Figure 10 shows endothermic process occurring exponentially along the reactor.

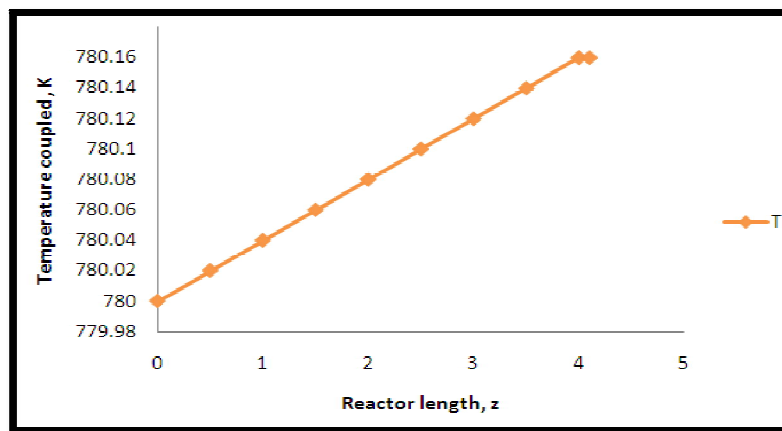


Figure 11: Steady State Variation of Temperature along Reactor Length [m]

Figure 11 indicates steady state temperature profile varying along the reactor. The reaction process occurring in the reformer reactor is endothermic process showing that heat is added to raise reaction temperature. The temperature increases as reactor length increases from $z=0\text{m}$ to $z = 4\text{m}$ and becomes steady at reactor 3 outlet end of reaction process.

5. Nomenclature

5.1. Symbols Meaning Units

- A Pre-exponential factor/frequency factor/Arrhenius constant A_0 or K_0
- LPG Liquefied Petroleum Gas
- ρ_i Density of chemical species i
- SS Sum of squares

F_0 Mass flow rate of gas-oil

- ρ_{cat} Mass density of catalyst
- R^2 Coefficient of determination
- CL Confidence limit
- λ Marquarrett-Levenberg parameter
- Δ Incremental value
- w_c Weight of catalyst
- θ_i Catalyst surface coverage
- r_i Rate of reaction of species, i , $\text{mol}/\text{m}^3\text{s}$
- P_i Partial pressure of species, i , atm
- τ 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 $i = \text{Naphthenes, paraffins, Aromatics}$
- RSS Regression Sum of Square
- $\Delta H_{r,i}$ Change in Heat of Reaction of species, $i = \text{N, P, A}$ & GkJ/Kmol

- Q Quantity of heat, KJ/s (KW)
- q Quantity of heat per unit volume KW/m³
- C_p Specific heat capacity of the system KJ/Kmol K
- u_f Superficial velocity, m/s
- U Overall coefficient of heat
- 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_{H₂} = mole fraction of Hydrogen; mol

r_i = rate of reaction for species, i, = (N, A, P, H₂, and G); mol/s

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

v_o = Volumetric flow rate; m³/s

A = Cross sectional area of the reactor; m²

P_T = 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

P_i = Partial pressure of species, i; atm

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

ΔV = Differential volume for a section in PFR; m³

Δz = Change in distance for the cross-section of the Plug flow reactor m

τ = Space time; seconds

C_T = Total concentration; mol/L

i = Naphthenes, Paraffins, Aromatics, Gases

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