

# Mechanism and Kinetics of Continuous Catalytic Cracking in Tubular Reactors

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**Abstract:**-The mechanism cum kinetics in continuous catalyst cracking reactions in tubular reactors is presented in this research explicates. The process chemistry stoichiometric balance on the feed materials was taken from fundamental principles material balance of the feed to derive models for investigation analytically; to obtain progressive depletions of feed with no catalyst effects on the process conditions in reactors. The reactor energy-temperature effects were obtained from the principles of conservation of energy. The two models were integrated numerically to achieve profiles on the feed depletion mechanisms and kinetics in the reactors. The deviations of the model predictions stood as follows 0.25, 0.42, 3.44, nil & 0.0001 respectively for paraffin, naphthenes, aromatics, and gas and Temperature.

**Keywords:** Mechanistic model, kinetics, feed-depletion, catalytic-reactors, Mass-Energy-model

## I. INTRODUCTION

Having employed some strenuous mathematical search to estimate activation energies  $E_i$ , rate constant forward reaction  $K_f$ , rate constant reverse reaction  $K_r$ , and equilibrium constant  $K_p$  of the reactions kinetic model; it is incumbent to operationalize research of the series-complex reactions taking place in the reformer reactors [Bommannam, Srivastava, & Saraf, 1989];

The feed lump naphtha cracking in the reforming reactors in series is a complex reactions chemistry [Weizmann, 1983]; [UOP, 1983]. Four major kinetics of the process were idealized and coupled with the reactor equations. The reactions kinetics considered were that of the dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffin to naphthenes, cracking of paraffin, and cracking of naphthenes for the estimation of reactions control parameters. These reactions were idealized to account for the reforming process in the researches posited by [Obobo, 2005]; [Wordu, 2009]; [Wordu & Akpa, 2014]; [Ojong & Wordu, 2018]; [Wordu & Ojong, 2018].

The idealized four main reactions were based on sound chemistry of lumping the subsidiary reactions [Smith, 1959]; [Jacob & Weekman, 1976]; [Coxon & Bischoff, 1987] for the synthesis of rate laws that describe the mass action velocity for the cracking processes of the feeds in the reactors, one top of the other with gravity mobile flow of catalyst from reactor 1 to reactor 3. The reactor/plant design or configurations

brings to barest minimum the deactivation of catalyst by the precursors of complex reactions [Nigerians PHRC Reactor plant, 1991].

The aromatic ring is quite stable during reforming process except side chains undergo de-alkylation and hydro-de-alkylation reactions on the aromatics which is the reformate gasoline analyzed having a required octane number range 90 to 94.

## II. MATERIALS AND METHOD

### 2.1 Continuous Catalytic Cracking Reactor model [CCCRM]

#### 2.1.1 Theoretical Concepts: Constraints/Assumptions

The derivation of the *Continuous Catalytic Cracking Reactor model [CCCRM]* model for this research maintains the following constraints are:

- **Continuous catalyst regeneration process in the regenerator section of the reactor system which keeps the catalyst at 100% efficiency**
- **The reactor is a stacked tubular 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  $C_6 - C_8$  hydrocarbons.**
- **Models maintain a lumping chemistry of the paraffin, Aromatics and Naphthenes.**
- **The Hydrogen recycle shall maintain 1.6 moles.**

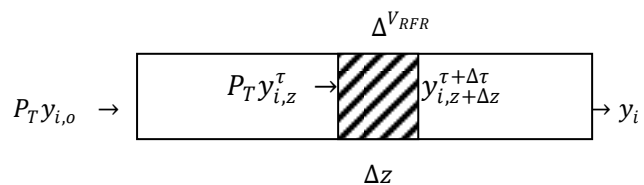


Figure 1 Schematics of Ideal flow reactor differential volume.

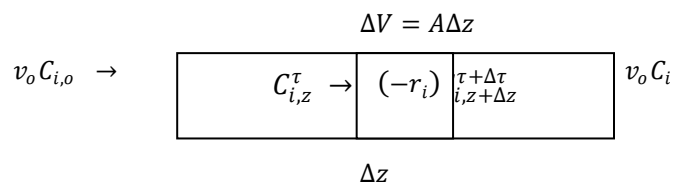


Figure 2 Mole fractions of feed varying along the differential volume.

Fundamental Material Balance

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

Equation [1] is developed under steady state process;

$$\left\{ \begin{array}{l} \text{Rate of accumulation} \\ \text{of species, i, within the} \\ \text{reactor} \end{array} \right\} = 0 \quad [2]$$

$$\left\{ \begin{array}{l} \text{Rate of inflow of} \\ \text{species, i, in the} \\ \text{flow reactor} \end{array} \right\} = v_o C_{i,z}^\tau \quad [3]$$

$$\left\{ \begin{array}{l} \text{Rate of outflow of} \\ \text{species, i, from the} \\ \text{flow reactor} \end{array} \right\} = v_o C_{i,z+\Delta z}^{\tau+\Delta\tau} \quad [4]$$

$$\left\{ \begin{array}{l} \text{Rate of depletion} \\ \text{of species, i, due to} \\ \text{chemical reaction} \\ \text{processes occurring} \\ \text{within the flow reactor} \end{array} \right\} = (-r_i)\Delta V \quad [5]$$

Combining equations [2] to [4] into equation [1]

$$\frac{dn}{d\tau} = v_o C_{i,z}^\tau - v_o C_{i,z+\Delta z}^{\tau+\Delta\tau} - (-r_i)\Delta V \quad [6]$$

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

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

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

Divide both sides by  $\Delta Z A$

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

$$\lim_{\Delta z \rightarrow 0} \frac{\Delta C_i}{\Delta z} = \frac{\partial C_i}{\partial z} \quad [6]$$

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

$$\frac{\partial C_i}{\partial \tau} + \frac{v_o}{A} \frac{\partial C_i}{\partial z} + (-r_i) = 0 \quad [7]$$

But,

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

From ideal gas equation

$$C_i = P_i/R_T \quad [8]$$

Thus,

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

$$\frac{1}{RT} \frac{\partial P_i}{\partial \tau} + \frac{v_o}{ART} \frac{\partial P_i}{\partial z} + (-r_i) = 0 \quad [9]$$

$$\frac{\partial P_i}{\partial \tau} + \frac{v_o}{A} \frac{\partial P_i}{\partial z} + RT(-r_i) = 0 \quad [10]$$

Again, Raoult stated mathematically,

$$y_i = P_i/P_T$$

$$P_i = P_T y_i \quad [11]$$

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

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

$$\frac{\partial y_i}{\partial \tau} + \frac{v_o}{A} \frac{\partial y_i}{\partial z} + C_T(-r_i) = 0 \quad [12]$$

At steady state;

$$\frac{\partial y_i}{\partial \tau} = 0$$

$$\frac{v_o}{A} \frac{dy_i}{dz} + C_T(-r_i) = 0 \quad [13]$$

But

$$\frac{v_o}{A} = \frac{F_{Ao}}{A} = L/\tau = u_f \quad [14]$$

$$u_f \frac{dy_i}{dz} + C_T(-r_i) = 0 \quad [15]$$

Equation [15] model for the material balance

## 2.2. Solution Techniques

$$\frac{dT}{dz} = \frac{1}{\mu_f} (-r_i) \quad [16]$$

$$\frac{dT}{dz} = \frac{1}{\mu_f C_{pp}} \{ \sum_{i=1}^5 (-r_i) (\Delta H_{r,i}) \} \quad [17]$$

**Fourth-order Runge-Kuta numerical algorithm for systems of ordinary differential equations mathematically demonstrated in details as:**

Equations [16] and [17] are assigned 1 and 2 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:

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

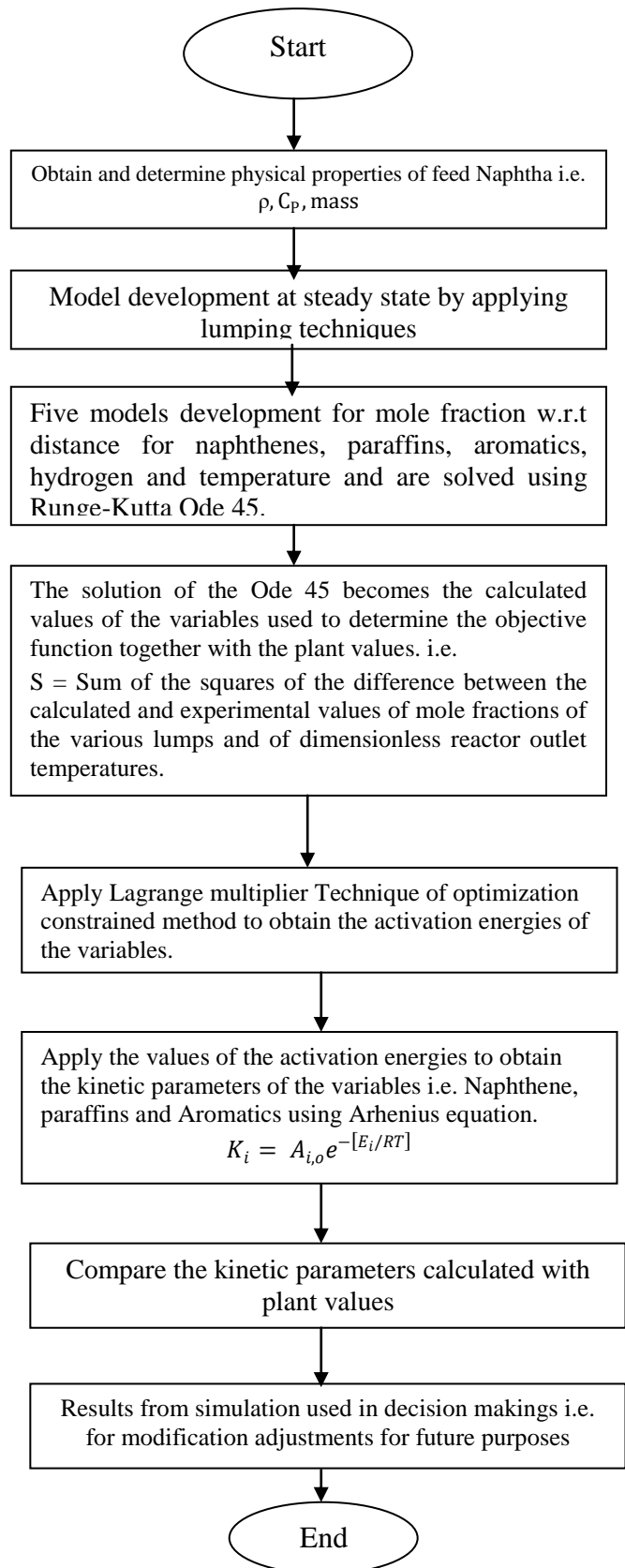
$$h = \text{step size}$$

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

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

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

Computational flow chart Mechanism cum Kinetics [CCCR M]



### III. RESULTS AND DISCUSSIONS

Table 1 Results for SSP Yield of Species of naphtha lump feed

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	0.3	0.282	0.569	5.26E-05	780.0774
2.5	0.265	0.24	0.681	6.63E-05	780.0978
3.0	0.202	0.201	0.793	8.00E-05	780.1181
3.5	0.198	0.193	0.905	9.37E-05	780.1385
4.0	0.15	0.145	1.000	1.08E-04	780.1589
4.1	0.105	0.104	1.000	1.09E-04	780.1629

Where, SSP = Steady-state process

Table 3 Comparison of Steady State Values and Plant Data

Species	Plant data	SS-values	Deviation
<b>Lumps</b>	<b>Mole</b>	<b>Mole</b>	$D = \frac{SSP - \text{Plant data}}{SSP}$
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

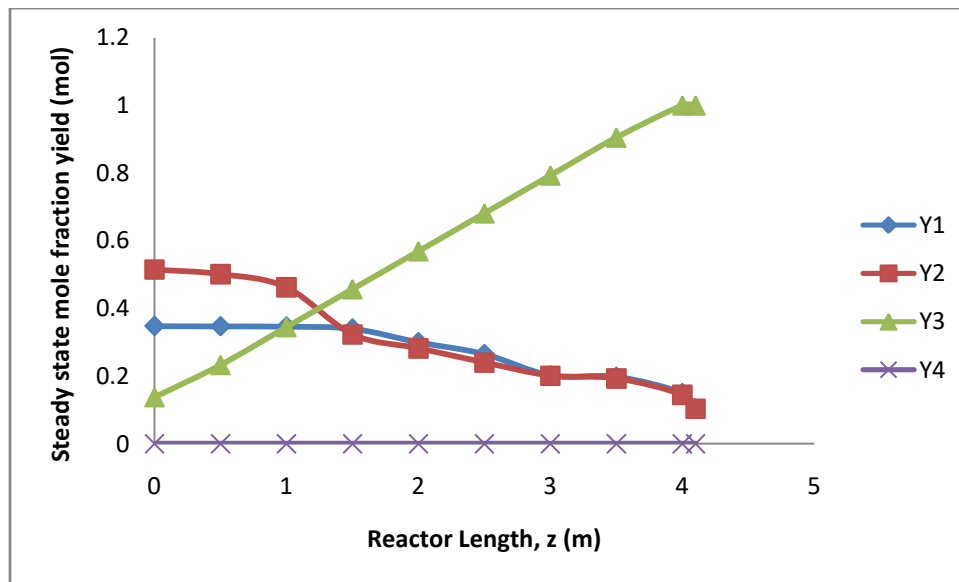


Figure1 Steady state yield of mole fraction of feeds along reactor length

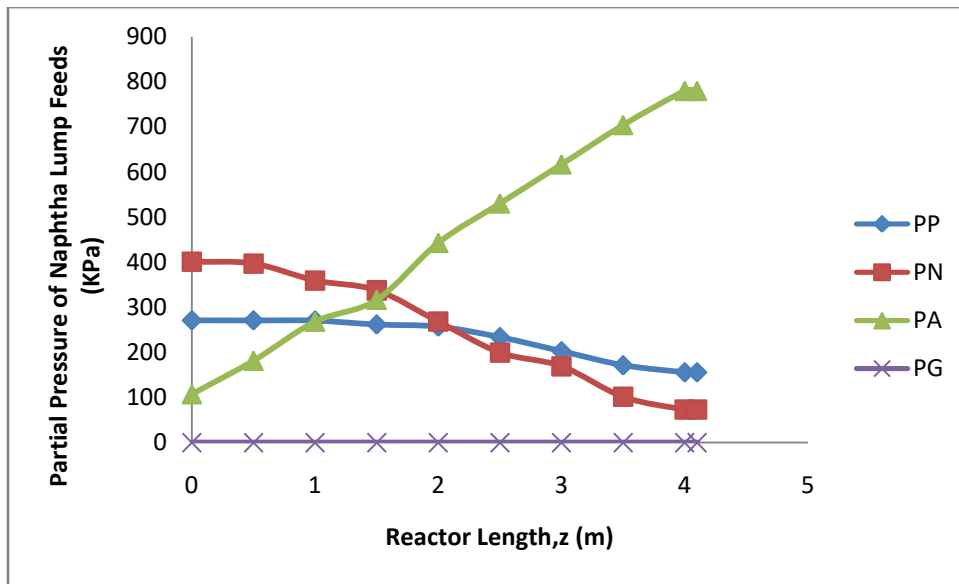


Figure 2 Composite plot of feed lumps depletions along reactor length

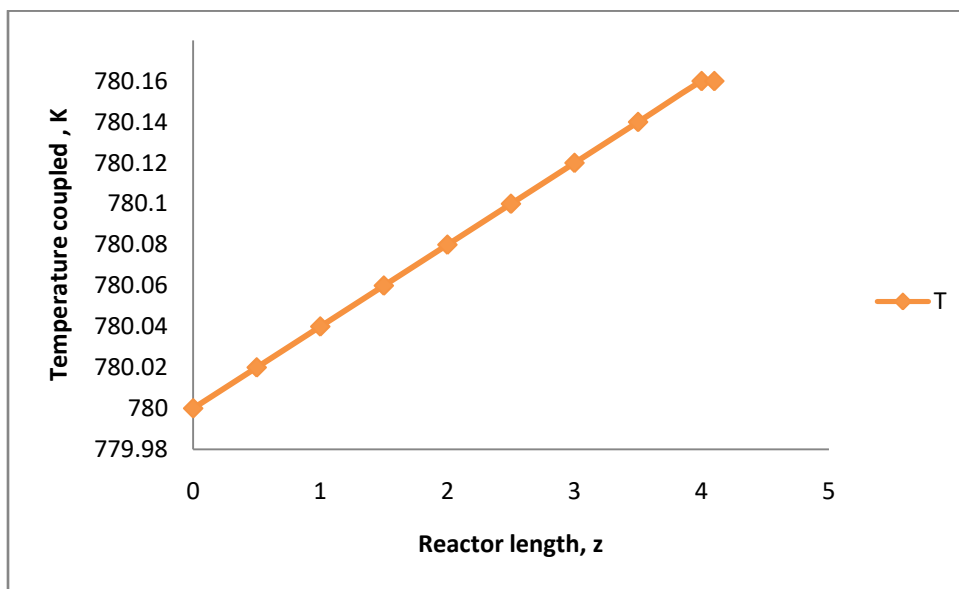


Figure 3 Variation of temperature along reactor length

#### IV. DISCUSSIONS

##### 4.1 Variations of mole fractions of feed lumps along the length of reactor

Figure 1 shows a steady state composite plot of the yields of the feed fractions in the lumped feed, cracking along the length of the tubular reactor 3 outlets. There is a progressive increase exponentially on the aromatics to a maximum value it tends to remain constant. Figure 1 delineates steady rate of production of gases methane, ethane, propane and butane along the length of the reactor arising as the cracking of the feed lumps progressed.

Figure 2 depicts a clear mechanistic and kinetics of the depleting process, with each lump showing a distinct spread out of its performance during cracking process in the reactor 3. The result of this cracking is therefore, proper utilization of molecular hydrogen for effective reforming reactions.

Figure 3 depicts the temperature profile of feed cracking actions along the length of the reformer reactors. The complex reaction process in the reactors is endothermic as more heat is needed for the process to start and continues to final stage reactor 3. The temperature initially starts from 780k and increases exponentially to 809k at reactor length of 4.1meters. Figure 3 shows that as the temperature increases the rate of

cracking progressed and more yields of products in gases and aromatics [gasoline reformat] is achieved.

Finally, perfect endothermic process is maintained, where the heat and/or enthalpy of the feed lumps increases [**H<sub>R</sub> is greater zero**] while [**Q is less than zero**] and **preheaters are used to maintain steady state heat for reforming of the feeds up to reactor 3 outlet temperature, 780K.**

## V. CONCLUSION

The research mathematical imaginative tendencies of studying the complex series-parallel change of feed lumps in reactors in series explicated. The kinetic expressions which avail the study were developed from the complex series-parallel reactions taking place in the reactors. The C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> gases are hybridized in good proportions as liquefied petroleum gas for domestic purposes.

Finally, more gases and aromatics being produced satisfy the economic balance of the design of reformer reactors in series.

## NOMENCLATURE

Symbols	Meaning	Units
$E_a$	Activation Energy	J/Kmol
$\Delta H$	Enthalpy Change	
$T$	Absolute Temperature	
$R$	Gas constant	KJ/Kmol K
$K^+$	Rate constant	
$A$	Pre-exponential factor/frequency factor or Arrhenius constant $A_0$ or $K_0$	
$LPG$	Liquefied Petroleum Gas ethane, propane and buthane	
$\rho_i$	Density of chemical species $i$	
$y_i$	Mole fraction of species, $i$	$i$
$r_i$	Rate of reaction of species, $i$	$i, mol/m^3s$
$P_i$	Partial pressure of species, $i$	$i kpa$
$\tau$	Space Time,	$s$
$C_T$	Total concentration	$mol/m^3$
$y_i$	Mole fraction of species $i$ , where $i$ = Naphthenes, Paraffins, Aromatics	
$V_0$	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
$U$	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	
$y_{H_2}$	= mole fraction of Hydrogen; mol	
$r_i$	= rate of reaction for species, $i$ , = (N, A, P, H <sub>2</sub> , 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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